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POHC ANALYSIS METHODS FOR HAZARDOUS WASTE INCINERATION

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Volume 2

by

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16. ABSTRACT The report gives preliminary data on methodology for two groups of compounds: organometallics and other organic compounds difficult to measure by the generalized methods. Previous work (Contract 68-02-2685, Task 111, and Task 1 of this contract) involved the evaluation of generalized GC/FID, GC/MS, and HPLC/UV methods for determining approximately 170 compounds from the approximately 400 compounds in Appendix VIII, Part 261, 40 CFR. However, the survey analysis portion of waste characterization often targets specific compounds for determination in incinerator effluent that are not amenable to previously developed methods. Therefore current research involves the development of specific GC/FID, GC/MS, and HPLC/UV methods for the determination of several of these compounds. Organometallic compounds such as benzenearsonic acid, hydroxydimethylarsine oxide (cacodylic acid), phenylmercury acetate, selenourea, and tetraethyl lead were selected as candidate POHCs for this study. In support of the destruction and removal efficiency requirement, generalized GC/FID, GC/MS, and HPLC/UV analysis methods were evaluated and, when necessary, modified for the determination of 33 additional candidate POHCs.

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Incinerators	Gas Chromatography	Stationary Sources		07D
Analyzing	Mass Spectroscopy	Principal Organic Hazardous Constituents	14B	
Organometallic Compounds	Ultraviolet Spectoscopy	Liquid Chromatography	07C	
Organic Compounds		Destruction and Removal Efficiency (DRE)	13L	
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FOREWORD

This report has been prepared by Southern Research Institute as part of ongoing studies in support of regulatory programs of Environmental Protection Agency's (EPA's) Air and Energy Engineering Research Laboratory, Research Triangle Park, North Carolina. This report contains criteria for the analysis methods for determination of principal organic hazardous constituents (POHCs) from the combustion of hazardous waste. The data in this report are intended as a reference to be used by laboratories that are monitoring the hazardous-waste streams of incineration facilities. Because of subtle differences among laboratories and analytical instrumentation, analysts who participate in similar studies should generate data that will establish their own criteria for the analysis of POHCs.

ABSTRACT

As part of the Resource Conservation and Recovery Act of 1976, the U.S. Environmental Protection Agency has proposed regulations for owners and operators of facilities that treat hazardous wastes by incineration to ensure that these incinerators will be operated in an environmentally responsible manner. The primary criterion upon which the operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator. The DRE value, defined in terms of waste-input and stack-output levels of designated principal organic hazardous constituents (POHCs), must be equal to or greater than 99.99%.

Approximately 400 compounds are included in Appendix VIII, Part 261, 40 CFR. Previous work (Contract 68-02-2685, Work Assignment 111 and Work Assignment 001 of this contract) involved the evaluation of generalized GC/FID, GC/MS, and HPLC/UV methods for the determination of approximately 170 compounds from this list of POHCs. However, the survey analysis portion of a waste-characterization scheme often targets specific compounds for determination in incinerator effluent that are not amenable to previously developed methods. Therefore, current research involves the development of specific GC/FID, GC/MS, and HPLC/UV methods for the determination of several of these compounds. This report presents preliminary data on methodology for two groups of compounds, organometallics and other organic compounds difficult to measure by the generalized methods.

Organometallic compounds such as benzenearsonic acid(I), hydroxydimethylarsine oxide (cacodylic acid)(II), phenylmercury acetate(III), selenourea(IV), and tetraethyl lead(V) were selected as candidate POHCs for this study. Tetraethyl lead was easily measured by the generalized GC/FID and GC/MS procedures. Selenourea required a new HPLC/UV option. The two organoarsenic compounds and the organomercury compound could not be determined by HPLC/UV with adequate sensitivity and were not easily determined by GC. We have demonstrated that iodide derivatives of compounds I, II, and III can be determined by GC/FID and GC/MS.

In support of the DRE requirement, we evaluated and, when necessary, modified generalized GC/FID, GC/MS, and HPLC/UV analysis methods for the determination of 33 additional candidate POHCs. These candidate POHCs represent a variety of compound types, including esters, chlorinated aromatics, aliphatic and aromatic amines, nitriles, organosulfur compounds, polynuclear aromatics, and heterocyclics.

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ABBREVIATIONS AND SYMBOLS

amu	Atomic Mass Unit
Appendix VIII	Hazardous Constituents List (40 C.F.R. Part 261)
C.F.R.	Code of Federal Regulations
DFTPP	Decafluorotriphenylphosphine
DNPH	Dinitrophenylhydrazine
DRE	Destruction and Removal Efficiency
EI	Electron Impact Ionization Mode
EPA	U.S. Environmental Protection Agency
g	Gram
GC	Gas Chromatography
GC/FID	Gas Chromatography/Flame-Ionization Detection
GC/MS	Gas Chromatography/Mass Spectrometry
h	Hour
HI	Hydroiodic Acid
HPLC	High-Performance Liquid Chromatography
HPLC/UV	High-Performance Liquid Chromatography/ Ultraviolet Spectrometry Detection
ID	Internal Diameter
is	Internal Standard
μg	Microgram (10^{-6}g)
μL	Microliter (10^{-6}L)
mg	Milligram (10^{-3}g)
mL	Milliliter (10^{-3}L)
mm	Millimeter (10^{-3}m)
MM5	Modified Method 5 Sampling Train
mol wt	Molecular weight
ms	Millisecond
m/z	Mass to Change Ratio
ng	Nanogram (10^{-9}g)
nm	Nanometer (10^{-9}m)
PAH(s)	Polynuclear Aromatic Hydrocarbon(s)
POHC(s)	Principal Organic Hazardous Constituent(s)
PIC(s)	Product(s) of Incomplete Combustion
QA	Quality Assurance
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RRF	Relative Response Factor
RSD	Relative Standard Deviation
SASS	Source Assessment Sampling System
SIM	Selected Ion Monitoring
s	Second
SD	Standard Deviation
SoRI	Southern Research Institute
TCDD	Tetrachlorodibenzo-*p*-dioxin
t_R	Retention Time
UV	Ultraviolet Spectroscopy
VOST	Volatile Organic Sampling Train

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SECTION 1

INTRODUCTION

REGULATORY REQUIREMENTS FOR THE INCINERATION OF HAZARDOUS WASTES

As part of the Resource Conservation and Recovery Act (RCRA), the U.S. Environmental Protection Agency (EPA) has promulgated proposed, interim, and final regulations for the owners and operators of facilities that treat hazardous wastes by incineration. The purpose of the regulations is to ensure that such incinerators are operated in an environmentally responsible manner. The regulations cover a range of activities, including operational performance standards, waste analyses, trial burns, monitoring and inspections, recordkeeping and reporting, and the establishment of emission-control criteria (1). The specific details for each incinerator facility are authorized by facility permits.

A criterion upon which all operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator. DRE is defined in terms of waste-input levels and stack-output levels of the potentially hazardous substances and must be greater than 99.99% for proper incineration. The substances from the list in Appendix VIII, Part 261, 40 CFR, have been designated as candidate principal organic hazardous constituents (POHCs), although many inorganic substances have also been included.

SAMPLING AND ANALYTICAL METHODS FOR HAZARDOUS-WASTE INCINERATION

As part of the supporting documentation for the permit writer and for the incinerator facility's owners and operators, the EPA has compiled a manual of methods for sampling and analysis for use in measuring the levels of POHCs in the various streams of an incinerator facility, including inlet wastes, stack gas, process waters, fly ash, and bottom ash. This manual is entitled "Sampling and Analysis Methods for Hazardous Waste Combustion" (2) and shall be referred to as the "Methods Manual" hereafter. This manual expands upon and augments the information in the "Guidance Manual for Evaluating Permit Applications for the Operation of Hazardous Waste Incineration Units" (3).

This Methods Manual is intended to be a resource document for the preparation and execution of a sampling-and-analysis plan for hazardous-waste incinerators. The specific procedures described are primarily in the form of brief descriptions with reference to other documents that contain highly detailed description methods. Existing collections of sampling-and-analysis methods documentation such as "Test Methods for Evaluating Solid Waste" (SW-846) or "Samplers and Sampling Procedures for Hazardous Waste Streams" (EPA-600/2-80-018) have not been directly incorporated into the manual but are incorporated by reference (4,5).

During trial burns at an incineration facility, the sampling and analysis methods will allow measurement of those POHCs expected to be present in the waste and products of incomplete combustion (PICs). Also during trial burns, the waste samples may be characterized with the methods to establish limits on the waste composition that may be incinerated. During routine facility operation, the incoming wastes will be analyzed periodically to ascertain whether the composition of the waste has changed. Carbon monoxide will be monitored continuously, as specified in the Methods Manual, to indicate the combustion efficiency of the process. Periodically, at the frequency not specified in the current regulations, the influent and effluent streams are to be tested to monitor compliance with the DRE criteria.

The overall strategy for waste characterization includes test procedures to determine the characteristics of the waste and analysis procedures to determine the composition of the waste. The Methods Manual includes test procedures for proximate, survey, and directed analysis. An overview of this analytical approach is shown in Figure 1. Our brief discussion here is limited to directed analysis because the modification of analytical methods applicable to the identification and quantification of POHCs is presently of primary interest to us.

The directed-analysis portion of the waste-characterization scheme provides both qualitative and quantitative data for the potentially hazardous constituents that might reasonably be expected to be present in the waste. Directed analysis does not involve screening every waste sample against the complete hazardous component list. A preliminary judgment is made as to the compounds or types of compounds that are likely to be present. The directed analysis then consists of the minimum set of analytical techniques that can be applied to the waste for qualitative identification and quantitative determination of the components that are actually present.

In practice, the results of the directed analysis will establish whether the waste contains the suspected pollutant and will demonstrate the concentration range at which the pollutant may be expected to be found. Directed analysis will also be used to confirm and quantify unexpected hazardous components identified in the survey analysis.

MODIFICATION OF DIRECTED-ANALYSIS METHODS

The Methods Manual recommends a variety of analytical techniques for the determination of the list of POHCs given in Appendix VIII, Part 261, 40 CFR. Whenever documentation was available to support the practice, the methods for the determination of organic compounds were written to incorporate a high-resolution analytical technique--fused-silica capillary gas chromatography--and a highly specific detection technique--mass spectrometry. Also, whenever possible, high-performance liquid chromatography (HPLC) was recommended for the

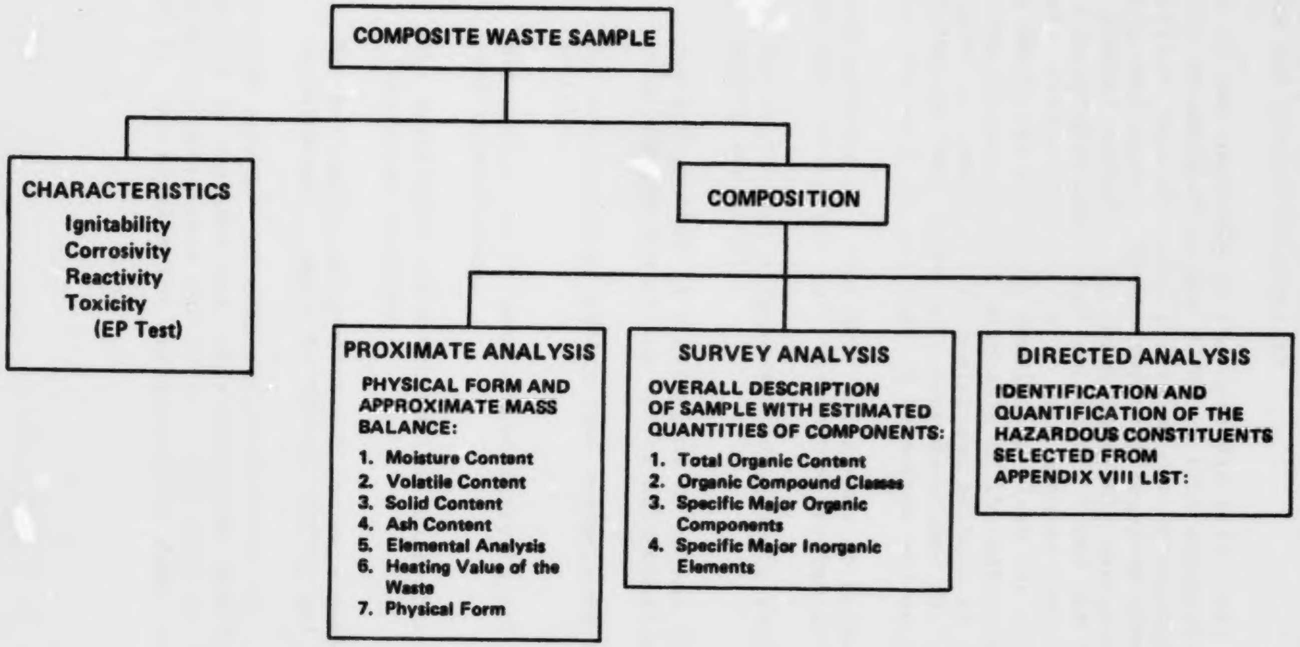

COMPOSITE WASTE SAMPLE
CHARACTERISTICS
Ignitability
Corrosivity
Reactivity
Toxicity
(EP Test)
COMPOSITION
PROXIMATE ANALYSIS
PHYSICAL FORM AND APPROXIMATE MASS BALANCE:
1. Moisture Content
2. Volatile Content
3. Solid Content
4. Ash Content
5. Elemental Analysis
6. Heating Value of the Waste
7. Physical Form
SURVEY ANALYSIS
OVERALL DESCRIPTION OF SAMPLE WITH ESTIMATED QUANTITIES OF COMPONENTS:
1. Total Organic Content
2. Organic Compound Classes
3. Specific Major Organic Components
4. Specific Major Inorganic Elements
DIRECTED ANALYSIS
IDENTIFICATION AND QUANTIFICATION OF THE HAZARDOUS CONSTITUENTS SELECTED FROM APPENDIX VIII LIST:

Figure 1. Overview of the analytical approach for waste characterization.

determination of organic compounds that could not be determined by gas chromatography with mass spectrometric detection (GC/MS). Many compounds are amenable to analysis by either procedure. The application of these two approaches to the determination of as many of the POHCs as possible was designed to provide satisfactory qualitative analyses on a cost-effective basis for a variety of waste types and process chemistries.

For some of the compounds on the Appendix VIII list, there were limited references that recommended either GC/MS or HPLC analyses. For some compounds, the only analytical methods readily available were colorimetric or thin-layer chromatographic techniques. Other compounds required chemical derivatization to produce a product suitable for chromatographic analysis. For yet other compounds, no acceptable analytical method was found for inclusion in the Methods Manual. Furthermore, GC/MS or HPLC methods were documented for some compounds for which the operating conditions given for analysis were peculiar to the compounds and not readily adaptable to the determination needed to reduce the number or complexity of analytical methods in the Methods Manual, generalized GC/MS and HPLC techniques were developed for the determination of as many of the chemicals on the list of hazardous wastes as possible.

The following specific tasks were undertaken to supplement the development of generalized test procedures and, in general, to improve the Methods Manual:

- The evaluation of generalized analysis methods for 13 POHCs by GC/FID and GC/MS.
- The application of a selective GC column and GC/MS using selected ion monitoring to the determination of 2,3,7,8-TCDD.
- The evaluation of generalized analysis methods for 25 POHCs by HPLC/UV.
- The evaluation of generalized analysis methods for 15 POHCs by HPLC/Fluorescence.
- The development of a derivatization technique for 3 organometallic POHCs.
- The evaluation of generalized analysis methods for 5 organometallic POHCs by GC/FID, GC/MS, and HPLC/UV.

The subsequent sections of this report describe the efforts by Southern Research Institute to evaluate and, when necessary, modify GC/MS and HPLC/UV generalized analysis procedures for POHCs. This work is presented in Sections 4 and 5. The results for organometallic POHCs are presented in Section 6.

SECTION 2

CONCLUSIONS

Generalized GC/FID, GC/MS, HPLC/UV, and HPLC/Fluorescence methods were developed for the determination of candidate POHCs. The candidate POHCs represent a variety of compound types, including esters, chlorianted aromatics, aliphatic and aromatic amines, nitriles, organosulfur compounds, polynuclear aromatics, heterocyclics, and organometallics.

A simple derivatization technique allows the determination of benzenearsonic acid, hydroxydimethylarsine oxide, and phenylmercury acetate by the generalized GC/FID and GC/MS procedures. These compounds were recovered from sorbents, filters, and water quantitatively. The derivatization procedure may be useful for other organometallic compounds. Compounds such as selenourea and tetraethyl lead may be determined by the HPLC/UV and GC/FID or GC/MS procedures respectively without major modifications of the procedures.

The determination of 2,3,7,8-TCDD by the general GC/MS procedure provides a screening analysis and may be applicable for survey-analysis of hazardous waste. However, ultimate selectivity and sensitivity are provided by an isomer-specific GC column and SIM mass spectrometry.

The developed generalized methods are suitable for inclusion in the POHC Methods Manual. The methods were standardized with selected organic compounds over concentration ranges of interest and showed acceptable precision in the determination of most of the compounds.

SECTION 3

RECOMMENDATIONS

Several recommendations for future investigations are as follows:

- SoRI will continue to apply the general survey methods to those POHCs not yet evaluated. We will review the new list of proposed compounds to be included in Appendix VIII.
- Based on SoRI findings, the proposed screening program should be evaluated when applied to incinerator-effluent samples, extracts, and sorbent media.
- In those cases where a generalized method was not sufficient to quantify a POHC, then more specific analytical techniques should be developed and evaluated on a priority basis.
- The applicability of generalized methods to the determination of products of incomplete combustion (PICs) will be evaluated.

SECTION 4

TECHNICAL APPROACH TO THE EXTENSION OF GENERALIZED ANALYSIS METHODS

GENERAL CONSIDERATIONS

The primary goal of our experimental work has been to develop generalized analytical methods for the determination of POHCs in appropriate organic solvents. Two basic chromatographic techniques were chosen: capillary gas chromatography (GC) and reversed-phase high-performance liquid chromatography (HPLC). During the development of the capillary GC methods, both flame-ionization detection (FID) and mass spectrometry (MS) were used to establish the techniques. During the development of the HPLC methods, we initially used ultraviolet (UV) detection. Fluorescence detection was also used to extend the method to compounds such as polynuclear aromatic hydrocarbons and aflatoxins.

In previous work (Work Assignment 001, Contract 68-02-3696 and Work Assignment 111, Contract 68-02-2685) we evaluated GC/MS and HPLC/UV methods for the determination of 70 and 100 POHCs, respectively. The methods were calibrated for candidate organic compounds over concentration ranges of interest and demonstrated acceptable precision in the determination of most of the compounds.

The work described in this report extends the coverage of the previous reports to an additional 13 POHCs by GC and 25 POHCs by HPLC/UV. Fifteen POHCs were determined using fluorescence detection in addition to UV detection. A detailed account of our findings is given in Section 5 of this report. A detailed account of our findings related to several organometallic compounds is given in Section 6 of this report.

SELECTION OF CANDIDATE POHCs

We selected candidate POHCs for analysis by GC and HPLC from the list of compounds in Appendix VIII (1). The compounds chosen were designated either as high-priority POHCs or as difficult-to-analyze POHCs. Seven high-priority organometallics were chosen by EPA for this study. Five were obtained from commercial sources and two were unavailable.

The generalized methods were also applied to an additional 33 compounds. Calibration curves, precision data, and detection estimations were obtained for these compounds.

PREPARATION OF STOCK STANDARD SOLUTIONS

We prepared stock standard solutions of the candidate compounds in appropriate solvents at a concentration of either about 2 mg/mL or about 10 mg/mL. These stock solutions were serially diluted as required to prepare working standards.

We used methylene chloride, hexane, methanol, or carbon disulfide as the solvent in the preparation of standards for GC/MS studies. Several different polar solvents (acetonitrile, methanol, and water) were used in the preparation of standards for HPLC determinations. The low solubility of some compounds in non-polar solvents required the use of more polar solvents to prepare standards.

GC ANALYSIS PROCEDURES

Description of Instruments and General Operating Conditions

We developed the GC/MS generalized test method on the Hewlett-Packard Model 5985 gas chromatograph/mass spectrometer-data system. The components of the instruments include a hyperbolic quadrupole mass filter with a convertible electron-impact (EI) and positive-ion chemical-ionization source and a capillary and jet separator GC/MS interface. It also has a data system that includes an HP2113 computer, a high-speed printer, a magnetic tape system, a 50-megabyte HP7920M disc drive system, a communications interface, GC/MS operating software, and an unabridged NBS spectral library. The supplemental GC/FID work was performed on a Hewlett-Packard Model 5840 gas chromatograph that was equipped for use with capillary columns.

The work with both the GC/MS and the GC/FID involved capillary column chromatography with matched, crosslinked fused-silica SE-54 capillary columns 25 m long, 0.31-mm ID. The initial operating conditions were chosen as a compromise of the conditions given for several capillary GC methods in the Methods Manual. The initial starting column temperature was 40 °C; the temperature was then programmed at 10 °C/min to 280 °C for 15 min. Alternate column temperature programs used rates of 20 °C/min and 30 °C/min. Injection and detection temperatures were 250 °C. The carrier gas was helium and was maintained at a flow rate through the column of about 2 mL/min. In both the GC/MS work and the GC/FID work, the "splitless" injection technique was employed. Consequently, we assumed that essentially all of the injected sample reached the column.

The determination of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) used a fused-silica capillary column capable of separating the 2,3,7,8-TCDD isomer from the other 21 TCDD isomers (Chrompack CP SIL 88, 0.22-mm ID, 60-m length). The initial column temperature was 45 °C for 3 minutes, then programmed to 190 °C at 25 °C/min, then programmed to 240 °C at 5 °C/min and held at 240 °C for 10 minutes. The injection temperature was 290 °C. Helium at 2 mL/min was used as the carrier gas. A 3-μL splitless injection was used instead of the 2-μL injection used in the generalized technique.

Optimization of the GC/FID and the GC/MS Procedures

GC operating conditions were optimized by analyzing solutions containing a variety of the candidate POHCs by the GC/FID technique. The column head pressure was adjusted appropriately to maximize the FID response to the test mixtures. We used these adjustments to pinpoint the optimum carrier-gas velocity.

Having established GC operating conditions by the GC/FID procedure, we then applied the method to the determination of the candidate POHCs by GC/MS. The mass spectrometer was operated in a full mass scanning range (41 to 450 amu) in the EI mode. The scan time was maintained at <1 s to enable the collection of enough scans to characterize each capillary GC peak. The mass spectrometer was used in the selected ion monitoring (SIM) mode to determine 2,3,7,8-TCDD. The ions monitored were m/z 257, 320 and 322 for native unlabeled 2,3,7,8-TCDD; 328 for $^{37}Cl_4$-2,3,7,8-TCDD; 332 and 334 for $^{13}C_{12}$-2,3,7,8-TCDD. Each ion was integrated for 70 ms for a total scan time of 420 ms.

GC Quality-Control Procedures

We calibrated the GC/FID and the GC/MS procedures with external standard solutions of the candidate POHCs. Five-point to eight-point calibration curves were prepared for each candidate POHC determined by gas chromatography. Each curve was a plot of the FID or the MS response (relative to anthracene-d_{10}) as a function of the quantity of the particular POHC injected on the GC column. Appendix A of reference 5 was used as a guideline for estimating detection limits for each candidate POHC. Step 1c, which is quoted below, was selected to develop the estimate of detection limit.

> The concentration value that corresponds to the region of the standard curve where there is a significant change in sensitivity at low analyte concentrations, i.e., a break in the slope of the standard curve.

The precision of determinations by GC/FID and GC/MS was determined by triplicate injections of at least one standard solution of each POHC investigated by gas chromatography. The estimate of precision of the replicate measurements is expressed as the relative standard deviation (RSD) calculated from Equation 1.

$$\text{RSD (\%)} = \left(\frac{SD}{\overline{X}}\right) 100 \qquad (1)$$

Standard Deviation (SD) was calculated from Equation 2.

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (X_1 - \overline{X})^2}{(n - 1)}} \qquad (2)$$

Mean relative response ($\overline{X}$) was calculated from Equation 3.

$$\overline{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \tag{3}$$

where

n = number of replicate measurements, and

X_i = relative reponse of the POHC standard.

Furthermore, we used anthracene-d_{10} as an internal standard in the GC methods. Along with the analytes, we injected anthracene-d_{10} to minimze the effect of injection volume and instrument performance upon the precision of determinations. Also, the anthracene-d_{10} internal standard was used to calculate the relative response factor (RRF) for each POHC from Equation 4.

$$RRF = (A_s C_{is})/(A_{is} C_s) \tag{4}$$

where

A_s = area of the characteristic ion for the POHC to be measured,

A_{is} = area of the characteristic ion for the internal standard,

C_{is} = concentration of the internal standard (μg/mL), and

C_s = concentration of the POHC (μg/mL) to be measured.

Recovery data were not applicable for this phase of the project because our analyses were done with neat solutions and standard mixtures of POHCs. We did not collect, prepare, or analyze field samples that required spiking of the matrix with surrogate standards or specific POHCs.

HPLC ANALYSIS PROCEDURES

We developed the generalized analysis procedures on a Hewlett-Packard Model 1084B high-performance liquid chromatograph equipped with a variable wavelength UV-VIS detector (190 to 600 nm), a variable volume injector, and an automatic sampling system. A Waters Associates Model 420-E filter fluorescence detector was used as an optional detector for selected POHCs. The following three bonded-phase columns were used with an acetonitrile/water eluent:

- Perkin-Elmer HC-ODS-Sil-X-1, 10-μm particle size, 25 cm long x 2.6-mm ID
- Waters Associates μ-Bondapak C_{18}, 10-μm particle size, 30 cm long x 3.9-mm ID
- Waters Associates μ-Bondapak CN, 10-μm particle size, 30 cm long x 3.9-mm ID

The Waters columns were employed only after we found that a few of the candidate POHCs either were not retained by or did not chromatograph well on the Perkin-Elmer column. It is reasonable to expect that columns from different sources may vary in retention and resolution characteristics. In addition, intralaboratory differences may occur that are attributed to the handling and history of the column.

Rather than attempt to establish one rigid set of HPLC operating conditions, our strategy was to try several separation mechanisms--adsorption, partition, reversed-phase, ion pairing, and ion suppression. Each system will allow determination of a broad range of compound types. We also investigated numerous isocratic and gradient elution programs with acetonitrile/water mobile phase. And we varied the wavelength of the UV detector or changed the excitation/emission filters of the fluorescence detector to optimize sensitivity.

Optimization and Calibration of the HPLC Procedures

The POHCs were grouped into classes of compounds and submitted for HPLC analysis. Initially, we analyzed standard mixtures of candidate POHCs to establish solvent programs suitable for the determination of a variety of compounds. At that time, the UV detector was set to monitor absorbances at 254 nm. Various chromatographic conditions were evaluated and modified until the elution rate of the resolution was optimized. Previous work (Work Assignment 111 of Contract 68-02-2685 and Work Assignment 001 of Contract 68-02-3696) led to the development of several HPLC options. Some of the options were not used in the present work. The various procedures (options) are:

Option 1 — Perkin-Elmer HC-ODS-SIL-X-1, 10-μm particle size, 25 cm long x 2.6-mm ID

Option 1A — Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, 5 min; 10 to 100% B in 35 min; 100% B, 10 min
Solvent Flow Rate: 1.0 mL/min

Option 1B — Solvent A: 1% (v/v) acetic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 10 min; 20 to 50% B in 20 min; 50% B, 10 min
Solvent Flow Rate: 2 mL/min

Option 1C — Solvent A: 1% (v/v) acetic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, 2 min; 10 to 100% B in 18 min
Solvent Flow Rate: 2 mL/min

Option 1D — Solvent A: 0.1 *M* acetate buffer in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, 2 min; 10 to 100% B in 18 min
Solvent Flow Rate: 1 mL/min

Option 1E — Solvent A: 0.005 *M* tetrabutylammonium phosphate in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 0 min; 20 to 100% B in 20 min
Solvent Flow Rate: 1 mL/min

Option 2 — Waters Associates μ-Bondapak C_{18}, 10-μm particle size, 30 cm long x 3.9-mm ID

Option 2A — Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 2% B, isocratic
Solvent Flow Rate: 1 mL/min

Option 2B — Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, 5 min; 10 to 100% B in 30 min
Solvent Flow Rate: 1 mL/min

Option 2C — Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 0 min; 20 to 100% B in 20 min; 100% B, 10 min
Solvent Flow Rate: 1 mL/min

Option 2D — Solvent A: 0.01 *M* pentane sulfonic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 10 min; 20 to 80% B in 20 min
Solvent Flow Rate: 1 mL/min

Option 3 — Waters Associates μ-Bondapak CN, 10-μm particle size, 30 cm long x 3.9-mm ID

Option 3A -- Solvent A: 1% (v/v) acetic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 0 min; 20 to 100% B in 20 min
Solvent Flow Rate: 1 mL/min

In subsequent work, the UV absorption spectra of the candidate POHCs were determined on a Cary Model 17 spectrophotometer to establish an absorption maximum in the range from 190 to 400 nm that would be a suitable alternate wavelength for quantifying each POHC by HPLC/UV.

As in the GC/FID analyses, a six- to eight-point calibration curve was prepared for each compound by plotting the absorbance (or emission) as a function of the injected quantity of the compound. An internal standard was not used in the HPLC/UV determinations.

HPLC/UV Quality-Control Procedures

The precision of determinations by HPLC/UV was estimated by replicate injections (n = 5) of the POHCs. In practice, not all POHCs will be found in a sample. Thus, after the POHCs in the sample are identified, an appropriate internal standard can be selected and then added to improve the quantification of POHCs.

SECTION 5

RESULTS AND DISCUSSION OF THE DEVELOPMENT OF ANALYSIS METHODS

GC/FID AND GC/MS ANALYSIS

We completed the determination of 13 POHCs by GC/FID and GC/MS. In Table 1 we present a summary of the GC/FID determinations of candidate POHCs. The retention time and on-column detection limit are given for each compound. The compounds are listed in the order of their elution from the GC column. Retention times are relative to that observed for the internal standard, anthracene-d_{10}. The on-column detection limit was estimated using the calibration curve as suggested in Appendix A of Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA 600/4-82-057, July 1982. Typical values were 0.7 to 50.0 ng. Reference chromatograms and calibration curves, which appear in Appendix A, are also cited in Table 1.

Appendix A contains chromatograms of individual POHCs and POHC mixtures. The chromatograms demonstrate the observed retention times, the peak shapes, and any shifts in the base line that occurred during the analysis. Although no two of the candidate POHCs may coexist in a field situation and, therefore, may not require simultaneous determination, the chromatogram of the compound mixture demonstrates the resolving power of the capillary column in general.

Each reference calibration curve given in Appendix A and cited in Table 1 is a point-to-point plot (solid line) of the FID response as a function of the quantity of the analyte injected onto the GC column. Each plot can be used to estimate the sensitivity expected in the determination of a particular analyte. In generating these curves, we made no attempt to determine the upper limit of the linear range of determinations. However, each plot demonstrates the linearity of the FID response within the range of quantities investigated. A laboratory that uses these methods will have to generate its own calibration curves, which may differ slightly from the ones given in this report. Our calibration curves will serve as a guide.

Also, with each calibration curve is the least-squares plot (a broken line) based on the linear-regression analysis of FID response versus concentration of analyte.

In Table 2, we summarize the GC/MS determination of candidate POHCs. As in Table 1, the retention times are given relative to the internal standard, anthracene-d_{10}. Table 2 also lists the five most abundant mass fragments of each compound and, moreover, specifies the mass of the ion of each compound that was used for the establishment of detection limits and for the generation of calibration curves. The detection limits were calculated from the calibration curves. Typical values of the detection limits were 1.0 to 80.0 ng.

TABLE 1. SUMMARY OF GC/FID DETERMINATIONS OF CANDIDATE POHCs

Compound	Relative retention time[a]	On-column detection limit, ng	Appendix A	
			Reference chromatogram	Reference calibration curve
Malononitrile	0.320	20	A-14	A-15
Hydroxydimethylarsine oxide[b]	0.324	12	A-6	A-7
Phenylmercury acetate[c]	0.471	1.0	A-6	A-8
Tetraethyl lead	0.570	0.7	A-20	A-21
1,3-Propane sultone	0.601	10	A-16	A-17
Benzenearsonic acid[d]	0.986	2	A-6	A-9
2-Acetylaminofluorene	1.24	3	A-1	A-2
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	1.26	0.7	A-18	A-19
7,12-Dimethylbenz(a)anthracene	1.52	20	A-1	A-3
Hexachlorophene	1.58	50	A-12	A-13
3-Methylcholanthrene	1.74	6	A-1	A-4
Dibenz(a,j)acridine	1.97	6	A-1	A-5
Dibenzo(a,i)pyrene	3.40	2	A-10	A-11

[a] Relative to the retention time of anthracene-d_{10}.

[b] Derivatized with HI to form dimethyl arsine iodide prior to injection.

[c] Derivatized with HI to form phenyl iodide prior to injection.

[d] Derivatized with HI to form benzene arsine iodide prior to injection.

TABLE 2. SUMMARY OF GC/MS DETERMINATIONS OF CANDIDATE POHCs

Compound	Relative retention time[a]	On-column detection limit, ng	mol wt	Masses of characteristic EI ions (relative abundance)					Appendix B		
				1	2	3	4	5	Reference chromatogram	Reference mass spectrum	Reference calibration curve
Malononitrile	0.269	20	66	66(100)	65(10)	64 (7)	67 (5)	50 (3)	B-22	B-23	B-24
Hydroxydimethylarsine oxide[b]	0.301	6	138	232(100)	217(62)	105(23)	89(15)	202(15)	B-19	B-20	B-21
Phenylmercury acetate[c]	0.460	9	337	204(100)	77(73)	51(52)	50(24)	127(17)	B-25	B-26	B-27
1,3-Propane sultone	0.565	5	122	58(100)	57(72)	122(48)	64(44)	-[d]	B-28	B-29	B-30
Tetraethyl lead	0.568	2	324	237(100)	295(73)	235(50)	208(47)	236(45)	B-34	B-35	B-36
Benzenearsonic acid[e]	0.975	6	202	279(100)	152(23)	151(12)	280 (8)	202 (6)	B-10	B-11	B-12
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	1.23	1	322	322(100)	320(78)	324(48)	257(25)	259(21)	B-31	B-32	B-33
2-Acetylaminofluorene	1.24	6	223	181(100)	180(79)	223(73)	152(26)	182(17)	B-1	B-2	B-3
7,12-Dimethylbenz(a)anthracene	1.51	10	256	256(100)	241(46)	239(41)	120(32)	240(29)	B-1	B-4	B-5
Hexachlorophene	1.52	80	404	198(100)	196(97)	209(73)	406(62)	210(55)	B-16	B-17	B-18
3-Methylcholanthrene	1.72	12	268	268(100)	126(65)	252(49)	253(38)	131(30)	B-1	B-6	B-7
Dibenz(a,j)acridine	1.96	6	279	279(100)	139(31)	280(26)	278(16)	125(15)	B-1	B-8	B-9
Dibenzo(a,i)pyrene	2.77	4	302	302(100)	303(30)	151(23)	300(22)	150(14)	B-13	B-14	B-15

[a] Relative to the retention time of anthracene-d_{10}.

[b] Derivatized with HI to form dimethyl arsine iodide, MW = 232, prior to injection.

[c] Derivatized with HI to form phenyl iodide, MW = 204, prior to injection.

[d] Only 4 ions detected.

[e] Derivatized with HI to form benzene arsine diiodide, MW = 406, prior to injection.

Reference total ion chromatograms, calibration curves, and mass spectra are cited in Table 2. The mass spectra are presented in Appendix B along with the reference chromatograms and calibration curves.

In Table 3, we present the results of triplicate GC/FID determinations of all of the candidate POHCs listed in Table 2. The calculated values of the standard deviation (SD) and relative standard deviation (RSD) in Table 3 indicate that most GC/FID determinations gave acceptable precision. The relative standard deviation ranged from 1% to 18%.

In Table 4, we present the results of triplicate GC/MS determinations of all of the POHCs listed in Table 2. In general, the precision of the GC/MS determinations were similar to the GC/FID determinations. The relative standard deviations ranged from 2% to 14%.

HPLC/UV ANALYSIS

General Considerations

We completed the determination of 25 POHCs by HPLC/UV. A summary of the results is given in Table 5. The retention time, on-column detection limit, and wavelength of detection are given for each POHC. The POHCs are listed by group in order of their elution from the HPLC column and subdivided by procedural option. Detection limits were calculated by the same procedure used in GC analyses. The wavelength of detection was 254 nm except where noted. An alternate wavelength was selected from the reference UV spectrum to optimize the detection of the POHCs.

Typical examples of HPLC/UV chromatograms and UV spectrum and standard calibration curves, which appear in Appendix C, are cross-referenced in Table 5. The chromatograms demonstrate the resolution and peak shape of each POHC, base-line drift, and any impurities or interferences present.

The UV spectra presented in Appendix C give the relative absorbance of each POHC. From the maximum absorption, alternate wavelengths other than 254 nm may be selected to increase sensitivity or selectivity of each POHC.

Each reference calibration curve given in Appendix C and cited in Table 5 is a point-to-point plot (solid line) of recorded UV response as a function of the quantity of POHC on the HPLC column. This quantity was calculated from the injection volume and the standard concentration. The calibration curve is shown by a solid line. Also included on each graph is the plot of the linear-regression equation calculated from the standard-curve data. This plot is shown by a broken line. Linear-regression analysis typically yielded correlation coefficients in excess of 0.9999.

TABLE 3. PRECISION OF GC/FID DETERMINATIONS

Compound	Quantity injected, ng	RRF[a] Mean	SD	RSD, %
2-Acetylaminofluorene	49.2	0.274	0.026	9.5
Benzenearsonic acid[b]	224	0.333	0.0049	1.5
Dibenz(a,j)acridine	49.4	0.273	0.028	10
Dibenzo(a,i)pyrene	34.8	0.238	0.027	11
7,12-Dimethylbenz(a)anthracene	45.2	0.0476	0.0084	18
Hexachlorophene	288	0.172	0.016	9.1
Hydroxydimethylarsine oxide[c]	81.0	0.0642	0.00086	1.3
Malononitrile	266	0.427	0.0082	1.9
3-Methylcholanthrene	47.5	0.290	0.020	7.0
Phenylmercury acetate[d]	222	0.136	0.0017	1.2
1,3-Propane sultone	184	0.0592	0.00055	0.9
2,3,7,8-Tetrachlorodibenzo-p-dioxin	23.7	0.0410	0.0017	4.0
Tetraethyl lead	12.6	0.406	0.0109	2.7

[a] $RRF = (A_s C_{is})/(A_{is} C_s)$

[b] Derivatized with HI to form benzene arsine iodide prior to injection.

[c] Derivatized with HI to form dimethyl arsine iodide prior to injection.

[d] Derivatized with HI to form phenyl iodide prior to injection.

TABLE 4. PRECISION OF GC/MS DETERMINATIONS

Compound	Quantity injected, ng	RRF[a]		
		Mean	SD	RSD, %
2-Acetylaminofluorene	24.6	0.317	0.00153	0.48
Benzenearsonic acid[b]	208	0.127	0.0033	2.6
Dibenz(a,j)acridine	24.7	0.606	0.066	10.8
Dibenzo(a,i)pyrene	52.0	0.450	0.043	9.6
7,12-Dimethylbenz(a)anthracene	22.6	0.0922	0.0061	6.6
Hexachlorophene	288	0.0374	0.0052	14
Hydroxydimethylarsine oxide[c]	40.6	0.353	0.032	9.1
Malononitrile	266	0.564	0.029	5.1
3-Methylcholanthrene	23.7	0.187	0.011	5.8
Phenylmercury acetate[d]	63.0	0.154	0.0068	4.4
1,3-Propane sultone	184	0.0680	0.0022	3.3
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	23.7	0.0284	0.0079	2.8
Tetraethyl lead	12.6	0.262	0.0011	4.2

[a] RRF = $(A_s C_{is})/(A_{is} C_s)$

[b] Derivatized with HI to form benzene arsine iodide prior to injection.

[c] Derivatized with HI to form dimethyl arsine iodide prior to injection.

[d] Derivatized with HI to form phenyl iodide prior to injection.

TABLE 5. SUMMARY OF HPLC/UV DETERMINATIONS OF CANDIDATE POHCs

Compound	Procedural option [a]	Retention time, min	Wavelength of detection, nm	On-column detection limit, μg	Appendix C		
					Reference HPLC chromatogram	Reference UV spectrum	Reference calibration curve
Selenourea	3A	3.4	254	0.2	C-68	C-69	C-70
Benzenearsonic acid	3A	3.4	263	6	C-16	C-17	C-18
Aflatoxin G-2	1A	13.2	365	0.03	C-13	C-14	C-15
Dimethyl phthalate	1A	14.0	254	0.1	C-28	C-29	C-30
Aflatoxin G-1	1A	14.1	365	0.07	C-10	C-11	C-12
Aflatoxin B-2	1A	14.2	365	0.03	C-7	C-8	C-9
Aflatoxin B-1	1A	15.0	365	0.07	C-4	C-5	C-6
Diethyl phthalate	1A	18.5	254	0.2	C-28	C-31	C-32
2-Acetylaminofluorene	1A	19.5	254	0.02	C-1	C-2	C-3
Naphthalene	1A	21.0	254	0.05	C-65	C-66	C-67
Butyl benzyl phthalate	1A	25.0	254	0.2	C-28	C-33	C-34
Di-*n*-butyl phthalate	1A	25.0	254	0.5	C-28	C-35	C-36
Fluoranthene	1A	26.8	254	0.005	C-56	C-57	C-58
Dibenz(a,j)acridine	1A	30.7	254	0.02	C-44	C-45	C-46
Benz(a)anthracene	1A	31.7	254	0.02	C-19	C-20	C-21
Chrysene	1A	33.0	254	0.02	C-41	C-42	C-43
7,12-Dimethylbenz(a)-anthracene	1A	34.0	254	0.2	C-53	C-54	C-55
Benzo(b)fluoranthene	1A	34.5	254	0.001	C-22	C-23	C-24
Bis(2-ethylhexyl) phthalate	1A	34.8	254	1	C-28	C-37	C-38
Di-*n*-octyl phthalate	1A	35.9	254	0.5	C-28	C-39	C-40
Benzo(a)pyrene	1A	36.6	254	0.01	C-25	C-26	C-27
Dibenz(a,h)anthracene	1A	37.0	254	0.05	C-47	C-48	C-49
3-Methylcholanthrene	1A	40.0	254	0.01	C-62	C-63	C-64
Indeno(1,2,3-c,d)pyrene	1A	40.0	254	0.02	C-59	C-60	C-61
Dibenzo(a,i)pyrene	1A	48.4	254	0.01	C-50	C-51	C-52

[a] See Section 4, pp. 11-13 for description of procedural options.

Each calibration curve can be used to estimate the sensitivity expected in the determination of a particular POHC. Each calibration curve demonstrates the linearity of response within the range of quantities investigated. We made no attempt to determine the upper limit of the linear range.

In Table 6, we present the results of replicate (n = 5) HPLC determinations of each POHC. The calculated values of the standard deviation (SD) and relative standard deviation (RSD) are given in the table. The relative standard deviations ranged from 0.3% to 2.3%.

HPLC/FLUORESCENCE ANALYSIS

General Considerations

We completed the determination of 13 POHCs by HPLC/Fluorescence. A summary of the results is given in Table 7. The retention time, on-column detection limit, and excitation/emission wavelengths are given for each POHC. The POHCs are listed by group in order of their elution from the column and subdivided by procedural option. The on-column detection limit was calculated in the same manner as used for GC/FID and GC/MS. The excitation wavelength was 280 nm for the PAHs (polynuclear aromatic hydrocarbons) and 360 nm for the aflatoxins. This was done by passing light from a Mercury Lamp through a 280-nm-narrow band-pass filter or a 360-nm-wide band-pass filter. The emission wavelength was >425 nm. This was done by measuring the emitted light through a 425-nm cut-off filter.

Because of the limitations of a fixed-wavelength fluorescence detector, alternate excitation/emission wavelengths were not selected.

Typical examples of HPLC/Fluorescence chromatograms and standard calibration curves, which appear in Appendix D, are cross-referenced in Table 7. The chromatograms demonstrate the resolution and peak shape of each POHC, base-line drift, and any impurities or interferences present.

Each reference calibration curve given in Appendix D and cited in Table 7 is a point-to-point plot (solid line) of recorded fluorescence response as a function of the quantity of POHC on the HPLC column. This quantity was calculated from the injection volume and the standard concentration. The calibration curve is shown by a solid line. Also included on each graph is the plot of the linear-regression equation calculated from the standard-curve data. This plot is shown by a broken line. Linear-regression analysis typically yielded correlation coefficients in excess of 0.9900.

Each calibration curve can be used to estimate the sensitivity expected in the determination of a particular POHC. Each calibration curve demonstrates the linearity of response within the range of quantities investigated. We made no attempt to determine the upper limit of the linear range.

TABLE 6. PRECISION OF HPLC/UV DETERMINATIONS

Compound	Quantity injected, µg	HPLC/UV response area counts x 10^{-3}		
		Mean	SD	RSD, %
2-Acetylaminofluorene	0.492	79.5	0.72	0.9
Aflatoxin B-1	0.188	67.4	0.41	0.6
Aflatoxin B-2	0.188	73.0	0.66	0.9
Aflatoxin G-1	0.188	50.0	0.41	0.8
Aflatoxin G-2	0.188	47.2	0.43	0.9
Benzenearsonic acid	12.4	198	3.7	1.8
Benz(a)anthracene	0.129	89.1	0.75	0.8
Benzo(b)fluoranthene	0.0225	74.7	0.71	1.0
Benzo(a)pyrene	0.252	289	3.0	1.0
Butyl benzyl phthalate	4.46	110	.97	0.9
Bis(2-ethylhexyl) phthalate	8.03	126	0.67	0.5
Chrysene	0.0948	98.9	2.2	2.3
Dibenz(a,j)acridine	0.176	71.7	1.2	1.6
Dibenz(a,h)anthracene	0.204	70.7	1.3	1.8
Dibenzo(a,i)pyrene	0.566	112	0.77	0.7
Di-n-butyl phthalate	4.14	102	0.26	0.3
Diethyl phthalate	4.50	138	0.90	0.6
7,12-Dimethylbenz(a)anthracene	0.212	73.2	0.36	0.5
Dimethyl phthalate	2.49	91.3	0.86	0.9
Di-n-octyl phthalate	7.67	121	0.89	0.7
Fluoranthene	0.256	88.1	0.73	0.8
Indeno(1,2,3-c,d)pyrene	0.123	72.3	1.0	1.4
3-Methylcholanthrene	0.198	88.8	0.42	0.5
Naphthalene	0.649	70.3	0.39	0.6
Selenourea	0.784	241.0	4.3	1.8

TABLE 7. SUMMARY OF HPLC/FLUORESCENCE DETERMINATION OF CANDIDATE POHCs

Compound	Procedural option [a]	Retention time, min	Wavelength of excitation, nm	Wavelength of emission, nm	On-column detection limit, µg	Appendix D Reference HPLC chromatogram	Appendix D Reference calibration curve
Aflatoxin G-2	1A	13.3	360	425	0.005	D-4	D-5
Aflatoxin G-1	1A	14.1	360	425	0.02	D-1	D-2
Aflatoxin B-2	1A	14.3	360	425	0.03	D-4	D-6
Aflatoxin B-1	1A	15.0	360	425	0.1	D-1	D-3
Fluoranthene	1A	27.6	280	425	0.02	D-19	D-20
Dibenz(a,j)acridine	1A	30.7	280	425	0.02	D-13	D-14
Benz(a)anthracene	1A	30.9	280	425	0.02	D-7	D-8
7,12-Dimethylbenz(a)-anthracene	1A	33.3	280	425	0.1	D-17	D-18
Benzo(b)fluoranthene	1A	34.2	280	425	0.001	D-9	D-10
Benzo(a)pyrene	1A	36.8	280	425	0.01	D-11	D-12
Dibenz(a,h)anthracene	1A	39.9	280	425	0.4	D-15	D-16
3-Methylcholanthrene	1A	40.4	280	425	0.03	D-23	D-24
Indeno(1,2,3-c,d)-pyrene	1A	40.9	280	425	0.02	D-21	D-22

[a] See Section 4, pp. 11-13 for description of procedural options.

In Table 8, we present the results of replicate (n = 6) HPLC fluorescence determinations of each POHC. The calculated values of the standard deviation (SD) and relative standard deviation (RSD) are given in the table. The relative standard deviation ranged from 0.1% to 3.5%.

Compounds Surveyed by GC or HPLC but not Completed

In Table 9, we list ten compounds which were surveyed by our generalized GC or HPLC methods. The compounds were either unstable on column or not retained by the columns used in the analysis. Additional method development will be required for the determination of these compounds. Compounds such as *n*-propylamine and methyl ethyl ketone should be analyzed as volatile compounds.

HPLC Methodology

A description of the generalized HPLC/UV analysis method including the various procedural options is presented in Section 4, page 12. We originally planned to analyze as many POHCs as possible by a generalized method using only one type of column (Reversed Phase C-18) and one solvent system (Acetonitrile/Water). This plan proved to be a very limiting approach. We therefore expanded the methodology to include other chromatographic techniques while still attempting to maintain the one-column type.

The first modification was the addition of acetic acid to the solvent system to suppress the formation of ionic species. Because reversed-phase chromatography achieves separation by different degrees of attraction of the sample for a non-polar stationary phase and a polar-mobile phase, reversed-phase chromatography is most useful with non-polar, non-ionic compounds. To separate ionic compounds by reversed-phase, one must make these compounds behave as non-ionic species with some non-polar (lipophilic) characteristics. If the pH of these systems is adjusted with a buffer, the ionic/non-ionic equilibrium is shifted toward the non-ionic species. This technique is called ionic suppression and is used for weak acids and bases with buffers in the 2 to 8 pH range. The POHC, in its non-ionic form, is then easily chromatographed. This was done in procedural options 1B and 1C. The same technique was used in Option 1D, with the addition of sodium acetate, buffered to a carefully controlled pH of 6.5. Sodium acetate was used rather than acetic acid because acetic acid gave a pH that was too low for the chromatographic separation of benzidines and similar structures.

Stronger organic acids and bases, however, cannot be separated by this technique. They remain ionic in the 2 to 8 pH range and, thus, are poorly retained or elute as skewed peaks. A technique called ion-pair chromatography uses an organic counter-ion in the mobile phase that forms a reversible ion-pair complex with the ionized sample. This complex behaves as an electrically neutral (non-ionic) and non-polar compound. Analyte retention on the column is influenced by the extent to which the ionized sample and the counter-ion form an ion-pair complex as well as the relative size of the non-polar group on the counter-ion.

TABLE 8. PRECISION OF HPLC/FLUORESCENCE DETERMINATIONS

Compound	Quantity injected, µg	HPLC/Fluorescence response area counts x 10^{-3}		
		Mean	SD	RSD, %
Aflatoxin B-1	0.250	126	2.4	1.9
Aflatoxin B-2	0.0625	835	7.3	0.9
Aflatoxin G-1	0.250	72.6	2.0	2.7
Aflatoxin G-2	0.0625	522	5.1	0.1
Benz(a)anthracene	0.387	302	3.8	1.2
Benzo(b)fluoranthene	0.0225	450	9.1	2.0
Benzo(a)pyrene	0.101	352	12.0	3.0
Dibenz(a,j)acridine	0.0618	414	3.1	0.8
Dibenz(a,h)anthracene	0.407	337	8.3	2.5
7,12-Dimethylbenz(a)anthracene	0.130	197	3.3	1.7
Fluoranthene	0.179	287	4.3	1.5
Indeno(1,2,3-c,d)pyrene	0.246	358	9.3	2.6
3-Methylcholanthrene	0.0989	321	11.3	3.5

TABLE 9. COMPOUNDS SURVEYED BY GENERALIZED GC OR HPLC METHODS BUT NOT COMPLETED

Compound	Technique	Comments
N-Nitroso-N-methylurea	GC, HPLC	Unstable on GC column - not retained on HPLC column
N-Nitroso-N-ethylurea	GC, HPLC	Unstable on GC column - not retained on HPLC column
N-Nitrosomorpholine	GC, HPLC	Unstable on GC column - not retained on HPLC column
n-Propylamine	GC	Not retained on GC column
Methacrylonitrile	GC	Not retained on GC column
Methyl ethyl ketone	GC	Not retained on GC column
N-Nitrosopyrrolidine	HPLC	Not retained on HPLC column
N-Nitrosomethylethylamine	HPLC	Not retained on HPLC column
N-Nitrosopiperidine	HPLC	Not retained on HPLC column
N-Nitrosodimethylamine	HPLC	Not retained on HPLC column

Because a few POHCs, even in their non-ionic form, have very little lipophilic characteristic, or are not chromatographed well by the C_{18} columns, we added to the generalized method a Waters μ-Bondapak CN column. The CN column is a highly versatile column used to separate both polar and non-polar compounds through normal phase (adsorption) and reversed-phase (partition) chromatography. And most solvents in the eluotropic series may be used in addition to both ionic suppression and ion-pairing techniques.

SECTION 6

ANALYSIS OF SELECTED ORGANOMETALLIC COMPOUNDS

GENERAL CONSIDERATIONS

The application of GC/FID, GC/MS, and HPLC/UV methods to the determination of selected organometallics was investigated. The specific compounds targeted were:

Benzenearsonic acid
Diethylarsine
Hydroxydimethylarsine oxide
Phenyldichloroarsine
Phenylmercury acetate
Selenourea
Tetraethyl lead

We were unable to find a source of diethylarsine and phenyldichloroarsine. The goal of this work was to apply the generalized chromatographic methods developed under Work Assignment 001, Contract 68-02-3696, to these compounds. Selenourea and tetraethyl lead were determined using minor modifications of the generalized methods. Benzenearsonic acid, hydroxydimethylarsine oxide, and phenylmercury acetate required derivatization prior to chromatography. The derivatization incorporated solvent removal, addition of hydroiodic acid, and extraction into hexane. The procedure used was a modification of that developed by Soderquist, et al. (6). Sorbent tubes, glass fiber filters, and water samples were spiked with organometallics to measure recoveries from materials used in stack sampling.

Derivatization Procedure

Standards were prepared by weighing small amounts (1.0 mg) of the three compounds into 50-mL centrifuge tubes, adding 1.0 mL of hydroiodic acid (HI) and shaking for 1 minute. The derivative was extracted into 10 mL hexane and diluted to make standards.

Sample Preparation: Sorbent Tubes

Sorbent tubes were prepared by packing 4-mm-ID glass tubes with ≈7.5 cm (400 mg) of XAD-2 resin (Applied Science 100/120 mesh) and with silanized glass-wool plugs, front and back. Triplicate tubes were spiked with aliquots of the organometallics in methanol. The first set of tubes was allowed to air dry for ≈1 hour before extracting with two 5-mL portions of methanol. The methanol extracts were combined in 50-mL centrifuge tubes and blown dry with a gentle stream of N_2. The residues were derivatized with 1 mL of hydroiodic acid (HI), and the derivatized organometallics were extracted into 10 mL of hexane. A blank (unspiked) XAD-2 sorbent tube was carried through the procedure with the spiked tubes.

Another set of tubes was packed, spiked, and allowed to sit for 3 days. The tubes were then extracted, and the extract was derivatized and analyzed in the same manner as above.

The last set of sorbent tubes was packed, spiked, and then allowed to sit for 1 hour. Warm, moist air (≈85% relative humidity) was then pulled through the tubes for 2 hours at a rate of ≈200 mL/min. A flask was placed at the exit end of the sorbent tube to trap condensate. The condensate in the flask was also analyzed for the organometallics.

Filter Samples

Glass-fiber filters (Gelman) were spiked in triplicate with 1-mL aliquots of a methanol solution of the organometallics (≈1 mg/mL). Filters were allowed to air-dry. Extraction of the filters with methanol was carried out in 200-mL screw-capped centrifuge bottles. The first triplicate set was extracted and analyzed the same day of spiking. Filters were extracted with two 10-mL portions of methanol shaking on a gyratory shaker for 10 min. The methanol extracts were dried with a gentle stream of N_2. The residues were derivatized with 1-mL of HI. The derivatized organometallics were extracted into 10.0 mL of hexane. A blank filter was carried through the procedure with the spiked filters. Another set of filters was spiked, allowed to sit 3 days, and then analyzed in the same manner.

Water Samples

Deionized water (50 mL) was spiked with 1-mg quantities of the organometallics. A 1-mL aliquot of HI was added to one sample. The derivatized water sample was then extracted with 20 mL of hexane. Another spiked water sample (50 mL) was dried to a residue using a gentle stream of nitrogen. This residue was then derivatized with a 1-mL aliquot of HI. The derivatized organometallics were then dissolved in 20 mL of hexane.

Standard Solutions of Tetraethyl Lead, Benzenearsonic Acid, and Selenourea

Standard solutions of tetraethyl lead were prepared in methylene chloride. Standard solutions of benzenearsonic acid and selenourea for HPLC/UV analysis were prepared in methanol.

Equipment

The GC/FID work was performed on a Hewlett-Packard Model 5840 gas chromatograph. GC/MS work was performed on a Hewlett-Packard Model 5985A gas chromatograph/mass spectrometer. Both instruments were equipped for split/splitless injections on capillary columns.

The HPLC/UV work was performed on a Hewlett-Packard Model 1084B HPLC with a variable-wavelength UV-VIS detector (190-600 nm) and an automatic sampling system.

Procedures

The generalized GC/MS, GC/FID procedure is listed below:

- Instruments: HP5985A GC/MS; HP5840 GC/FID
- Columns: Two matched SE-54 bonded-fused-silica capillary columns, 0.32-mm ID, 25-m length
- Carrier gas: Helium, 30 cm/s (2 mL/min)
- Injection: 2 µL splitless
- Column temperature program: 40 to 280 °C at 10 °C/min, hold 15 min
- Injection temperature: 250 °C
- FID temperature: 250 °C
- MS parameters: Scan 41 to 450 amu/s. Electron ionization at 70 eV. Source temperature set to 200 °C. Capillary column plumbed directly into the ion source.

The initial operating conditions chosen were a synthesis of conditions that would allow the separation and detection of as many compounds as possible. Modifications of temperatures and rates may be necessary or desirable to optimize the analysis for specific compounds.

The HPLC/UV procedure is listed below:

- Instrument: HP1084B with a variable wavelength UV-VIS detector
- Column: Waters µ-Bondapak-CN, 10-µm particle size, 3.9-mm ID, 30-m length
- Solvents: A = 1% acetic acid in distilled deionized water B = acetonitrile
- Gradient Program: 10% B for 5 min, 10 to 100% B in 30 min, hold at 100% B for 5 min. Flow rate of 1 mL/min.

Optimization of the GC/FID and GC/MS Procedures

GC operating conditions were optimized by analyzing solutions containing organometallic POHCs by the GC/FID technique. The column-head pressure was adjusted appropriately to maximize the FID response to the test mixtures. We used these adjustments to pinpoint the optimum carrier-gas velocity.

GC Quality-Control Procedures

We calibrated the GC/FID and GC/MS procedures with standard solutions of the candidate POHCs. Five-point to eight-point calibration curves were prepared for each organometallic determined by gas chromatography. Each curve was a plot of the FID or MS response (relative to anthracene-d_{10}) as a function of the quantity of the particular POHC injected on the GC column. The detection limit for each organometallic was estimated from the calibration curve by the same method discussed in Section 4, p. 9. We also established mass spectra for the identification of the individual POHCs.

The precision of determinations by GC/FID and GC/MS was estimated by triplicate injections of at least one standard solution of each POHC investigated by gas chromatography. The estimate of precision of the replicate measurements is expressed as the relative standard deviation (RSD). The mean relative response, standard deviation, and RSD were calculated as described in "GC Quality-Control Procedure," pp. 9 and 10.

Furthermore, we used anthracene-d_{10} as an internal standard in the GC methods. Along with the analytes, we injected anthracene-d_{10} to minimize the effect of injection volume and instrument performance upon the precision of determinations. Also, the anthracene-d_{10} internal standard was used to calculate the relative response factor (RRF) for each POHC from Equation 4, p. 10.

HPLC/UV Quality-Control Procedures

The precision of determinations by HPLC/UV was estimated by replicate injections (n = 5) of benzenearsonic acid and selenourea. After the POHCs in the sample are identified, an appropriate internal standard can be selected and then added to improve the quantification of POHCs.

As in the GC/FID analyses, a five-point calibration curve was prepared for each compound by plotting the absorbance as a function of the injected quantity of the compound. An internal standard was not used in the HPLC/UV determination.

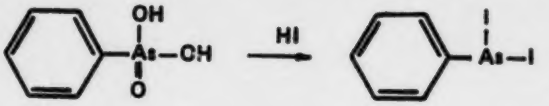
RESULTS AND DISCUSSION

Organometallics

The five organometallic compounds targeted required three different methods of analysis. The general GC/FID and GC/MS methods were used to determine tetraethyl lead(V). Benzenearsonic acid(I), hydroxydimethylarsine oxide(II), and phenylmercuric acetate(III) were derivatized with hydroiodic acid to improve thermal stability and volatility. Selenourea(IV) and benzenearsonic acid(I) were determined by HPLC/UV.

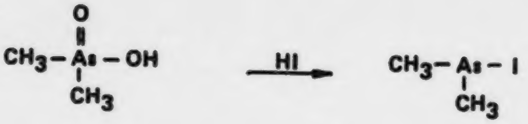
The hydroiodic acid derivatization procedure is similar to the procedure used by Soderquist (6). The following chemical equations describe the derivatization process for the three organometallics:

a.



(1)

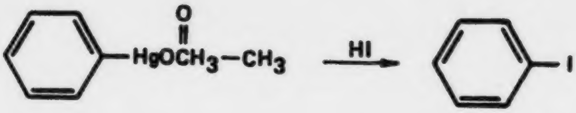
b.



$$CH_3-\overset{\overset{O}{\|}}{\underset{\underset{CH_3}{|}}{As}}-OH \xrightarrow{HI} CH_3-\underset{\underset{CH_3}{|}}{As}-I$$

(2)

c.



(3)

The reactions appear to proceed rapidly and quantitatively.

The general GC/FID and GC/MS procedures were used to determine the derivatives.

In Table 10 we present the GC/FID and GC/MS relative retention times and estimated on-column detection limits for compounds I, II, III, and V. The on-column detection limit was estimated from the calibration curve. Typical values ranged from 0.7 to 11.8 ng for GC/FID and from 1.5 to 8.8 ng for GC/MS. In Table 11 we list the five most abundant mass fragments of the compounds or compound derivatives reported in this study. The absolute intensity of the base peak in the mass spectrum was used to develop calibration curves. The precision of replicate determinations for GC/FID and GC/MS is presented in Table 12.

HPLC/UV

In Table 13 we present the retention times, on-column detection limits, and wavelengths of detection of the two POHCs determined by HPLC/UV. The high detection limit for benzenearsonic acid indicates that the HI derivatization method is the method of choice. Selenourea is easily determined by the HPLC/UV method presented in experimental section.

TABLE 10. SUMMARY OF GC/FID AND GC/MS DETERMINATIONS OF CANDIDATE POHCs

Compound	GC/FID				GC/MS			
	Reference chromatogram Figure No.	Reference calibration curve Figure No.	Relative retention time[a]	On-column detection limit, ng	Reference chromatogram Figure No.	Reference calibration curve Figure No.	Relative retention time[a]	On-column detection limit, ng
Benzenearsonic acid (HI derivative)	A-6	A-9	0.986	2	B-10	B-12	0.975	6
Hydroxydimethyl-arsine oxide (HI derivative)	A-6	A-7	0.324	12	B-19	B-21	0.301	6
Phenylmercuric acetate (HI derivative)	A-6	A-8	0.471	1	B-25	B-27	0.460	9
Tetraethyl lead	A-20	A-21	0.570	0.7	B-34	B-36	0.568	2

[a] Relative to the retention time of anthracene-d_{10}.

TABLE 11. PRECISION OF RELATIVE RESPONSE FACTORS FOR GC/FID AND GC/MS DETERMINATIONS[a]

	GC/FID			GC/MS		
Compound	Quantity injected, ng	Mean (n = 3)	RSD%	Quantity injected, ng	Mean (n = 3)	RSD%
Tetraethyl lead	12.6	0.406	3	12.6	0.262	4
Benzenearsonic acid (HI derivative)	224	0.333	1	208	0.127	2.6
Hydroxydimethylarsine oxide (HI derivative)	81	0.064	1	40.6	0.353	9
Phenylmercury acetate (HI derivative)	222	0.136	1	63.0	0.154	4

[a] RRF = $(A_s C_{is})/(A_{is} C_s)$

TABLE 12. SUMMARY OF CHARACTERISTIC EI IONS AND RELATIVE ABUNDANCES OF CANDIDATE POHCs

Compound	Mol wt.	Characteristic EI Ions derivatives (relative abundance) 1	2	3	4	5
Tetraethyl lead	324	237(100)	295(73)	235(50)	208(47)	236(45)
Benzenearsonic acid (HI derivative)	202[a]	279(100)	152(23)	151(12)	280 (8)	202 (6)
Hydroxydimethylarsine oxide (HI derivative)	138[b]	232(100)	217(62)	105(23)	89(15)	202(15)
Phenylmercury acetate (HI derivative)	337[c]	204(100)	77(73)	51(32)	50(24)	127(17)

[a] Molecular weight of HI derivative = 406

[b] Molecular weight of HI derivative = 232

[c] Molecular weight of HI derivative = 204

TABLE 13. SUMMARY OF HPLC/UV DETERMINATION OF CANDIDATE POHCs

Compound	Retention time, min	On-column detection limit,[a] μg	Precision summary			Appendix C	
			Quantity injected, μg	Mean area counts x 10^{-3}	RSD, %	Reference chromatogram	Reference calibration curve
Selenourea[b]	3.5	0.0123	0.784	241	4.3	C-68	C-70
Benzenearsonic acid[c]	4.1	1.14	12.4	198	1.8	C-16	C-18

[a] Estimated from the calibration curve.

[b] Wavelength of detection = 254 nm.

[c] Wavelength of detection = 263 nm.

Laboratory Recovery of Organometallics from Amberlite XAD-2 Resin, Glass-Fiber Filters, and Water

The sampling methods required for the ultimate analysis of POHCs in hazardous wastes and incinerator effluents during trial burns will vary according to the nature of the wastes. Prior to incineration, the hazardous waste may be a solid, liquid, slurry, or sludge. After incineration, the POHCs may be found in bottom ash, fly ash/electrostatic precipitator (ESP) catches, scrubber water, or stack gas.

Sampling of the effluent streams of a hazardous-waste incinerator serves several purposes. During trial burns, the measurement of POHCs in the stack-gas effluent is an integral part of the calculation of DRE values to determine if the incinerator meets its performance criteria. The sampling of stack-gas components is important to the process of obtaining permits for hazardous waste incinerators. Some of the sampling methods available to collect volatile POHCs at low concentrations in stack gas are the Modified Method 5 (MM5) sampling train, the Source Assessment Sampling Systems (SASS), and the Volatile Organic Sampling Train (VOST). These systems use specific sorbents to collect POHCs. We selected XAD-2 resin, a general purpose sorbent for organic compounds, to determine the recovery of POHCs from the sorbent. We also used glass-fiber filters and distilled deionized water to examine recovery from other parts of the sampling system. Methanol was used to extract benzenearsonic acid, hydroxydimethylarsine oxide, and phenylmercury acetate from the XAD-2 resins and glass-fiber filters. Water samples were evaporated to dryness prior to derivatization. Methylene chloride was used to extract tetraethyl lead. The determination of the analytes was performed by GC/FID or GC/MS. Figure 2 is a diagram of one of the XAD-2 tubes used. The XAD-2/moist-air experiment was performed 6 times. One tube showed significant water condensation. The water was evaporated to dryness and the residue was derivatized; the sum of the amounts found in the condensate and the XAD-2 resin was comparable to the other five determinations. Additional XAD-2 tubes were spiked and extracted after approximately one hour and spiked and extracted after approximately 72 hours. Table 14 presents the recoveries of the three organometallics from the XAD-2 resin experiments. In a separate experiment, tetraethyl lead was spiked onto XAD-2 tubes, exposed to moist air, and extracted with methylene chloride. Table 14 also presents the data from the tetraethyl lead tubes.

Three organometallics were also spiked onto glass-fiber filters, extracted with methanol, derivatized, and analyzed by GC/FID. The recovery data are presented in Table 15 for three spiked filters.

Because the three compounds were known to be somewhat water soluble, the compounds were spiked into 50 mL of distilled deionized water. Two experiments were performed. First, hydroiodic acid was added to the spiked water, the water was extracted with hexane, and then the extract was analyzed by GC/FID. Recoveries of hydroxydimethylarsine oxide and benzenearsonic acid were less than 3% and of phenylmercury acetate were greater than 100%. Second, the compounds were spiked into 50 mL of distilled deionized water, evaporated to dryness, derivatized, and dissolved in hexane, and the hexane was analyzed by GC/FID. The recovery of hydroxydimethylarsine oxide was 68%, of benzenearsonic acid was 87%, and of phenylmercury acetate was 83%.

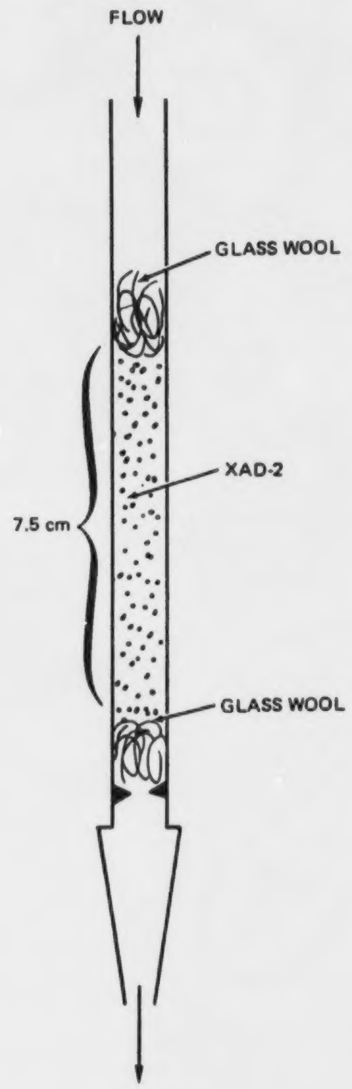

FLOW
GLASS WOOL
XAD-2
7.5 cm
GLASS WOOL

Figure 2. XAD-2 sorbent tube.

TABLE 14. RECOVERY OF POHCs FROM XAD-2 RESIN

Compound	Extracted after 1 hour			Extracted after 72 hours			Extracted after moist-air exposure		
	Amount added, μg	Avg % recovery (n = 3)	% RSD	Amount added, μg	Avg % recovery (n = 3)	% RSD	Amount added, μg	Avg % recovery (n = 6)	% RSD
Benzenearsonic acid	252	100	2.4	292	84	7.0	$245^{a,b}$ 315^{b}	104	10
Hydroxydimethylarsine oxide	278	92	7.8	278	69	8.7	300^{b} 318^{b}	82	16
Phenylmercury acetate	222	54	6.3	222	65	3.1	252^{b} 300^{b}	76	8
Tetraethyl lead[c]							248	91^{d}	3

[a] One sample had significant water breakthrough. Combination of the derivatives of the liquid and XAD-2 extracts were analyzed.

[b] A set of three samples was analyzed.

[c] Only the moist air exposure experiment was performed.

[d] n = 3.

TABLE 15. RECOVERY OF POHCs FROM GLASS-FIBER FILTERS AFTER 72 HOURS

Compound	Amount added, µg	Avg % recovery, (n = 3)	% RSD
Benzenearsonic acid	252	114	3.2
Hydroxydimethylarsine oxide	278	99	4.2
Phenylmercury acetate	222	97	4.6

Conclusions

A simple derivatization technique allows the determination of benezenearsonic acid, hydroxydimethylarsine oxide, and phenylmercury acetate by the general GC/FID and GC/MS procedures. These compounds were recovered from materials used in stack sampling quantitatively. The derivatization procedure may be useful for other organometallic compounds. Compounds such as selenourea and tetraethyl lead may be determined by the HPLC/UV and GC/FID or GC/MS procedures respectively without major modifications of the procedures.

SECTION 7

QUALITY-ASSURANCE SUMMARY

The work that was done at SoRI and presented in this report was performed under SoRI Quality Assurance plan for Contract 68-02-3696, Work Assignment 001, Amendment 001, September 21, 1983. Although the project includes environmentally related measurement activities, SoRI was not involved in field sampling or the preparation of field samples for analysis. Thus, sampling procedures, chain-of-custody procedures, and spiked-sample matrixes were considered as non-applicable in the systematic review of this project. The major efforts of SoRI were to evaluate and, when necessary, modify GC/MS and HPLC/UV generalized analysis procedures for candidate POHCs. This task was accomplished with individual POHCs and mixtures of POHCs. DFTPP was not run daily as specified in the QA project plan.

An internal audit of the project revealed no deficiencies in the internal quality-control checks and data processing. The relative retention times, on-column detection limits, chromatograms, calibration curves, relative ion abundances, spectra, and relative standard deviations in this report will be a guide for other analytical laboratories. Because of subtle differences among laboratories and analytical instrumentation, analysts who participate in similar studies should generate data that will establish their own criteria for the analysis of POHCs.

SECTION 8

PROJECT SUMMARY

EPA compiled a manual entitled "Sampling and Analysis Methods for Hazardous Waste Combustion," February 1984, which is intended to be a resource document for the preparation and execution of a sampling-and-analysis plan for hazardous-waste incinerators. The Methods Manual recommends a variety of analytical techniques for the determination of POHCs. Methods were written to incorporate fused-silica capillary gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC). These methods were designed to provide satisfactory qualitative and quantitative analyses on a cost-effective basis for a variety of waste types and process chemistries. Generalized GC/MS and HPLC techniques were developed for the determination of as many of the POHCs as possible.

We structured our laboratory work to lead systematically from the determination of the feasibility of developing generalized test methods to the standardization of the resulting methods for selected POHCs. Initially, we performed analyses of standard solutions of mixtures of selected POHCs to optimize instrumental operating conditions. Then we obtained individual chromatograms (GC/FID, GC/MS, HPLC/UV, and HPLC/Fluorescence), established calibration curves, and estimated limits of detection. The technical approach in the development and evaluation of the generalized instrumental methods is discussed in this report. The chromatograms and data are provided in three appendixes of this report.

Appendix A contains the chromatograms and calibration curves for the GC/FID determinations. Appendix B shows the mass spectra in addition to the chromatograms and calibration curves for GC/MS determinations. Appendix C contains the UV absorption spectra as well as the chromatograms and calibration curves for HPLC/UV determinations. Appendix D contains the chromatograms and calibration curves for HPLC/Fluorescence determination.

The following specific tasks were undertaken to supplement the development of generalized test procedures and, in general, to improve the Methods Manual:

- The evaluation of generalized analysis methods for 13 POHCs by GC/FID and GC/MS.
- The application of a selective GC column and GC/MS using selected ion monitoring to the determination of 2,3,7,8-TCDD.
- The evaluation of generalized analysis methods for 25 POHCs by HPLC/UV,
- The evaluation of generalized analysis methods for 15 POHCs by HPLC/Fluorescence.

- The development of a derivatization technique for 3 organometallic POHCs.

- The evaluation of generalized analysis methods for 5 organometallic POHCs by GC/FID, GC/MS, and HPLC/UV.

The preceding sections of this report describe the efforts by Southern Research Institute to evaluate and, when necessary, modify GC/MS and HPLC generalized analyses procedures for POHCs. This work is presented in Sections 4 and 5. The results for organometallic POHCs are presented in Section 6. Section 7 is the QA summary.

We believe that these data are encouraging. They should be the foundation for the design of more comprehensive studies of sampling, sample preparation, and sample analysis in support of the program for incineration of hazardous waste.

SECTION 9

REFERENCES

1. Resource Conservation and Recovery Act, Subtitle C §§3001-3013, 42 N.S.C. §§6921-6934, 1976, and Supplement IV, 1980.

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3. Vogel, G.; Brooks, K.; Cross, J.; Frankel, I.; Haus, S.; and Jacobsen, W. Guidance manual for evaluating permit applications for the operation of hazardous waste incinerator units. Final Report, EPA Contract 68-01-6092, U.S. Environmental Protection Agency, Washington, D.C.; 1981 April.

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APPENDIX A

CHROMATOGRAMS AND CALIBRATION CURVES FOR GC/FID DETERMINATIONS

Index

Compound	Reference chromatogram Figure No.	Reference calibration curve Figure No.
2-Acetylaminofluorene	A-1	A-2
Benzenearsonic acid	A-6	A-9
Dibenz(a,j)acridine	A-1	A-5
Dibenzo(a,i)pyrene	A-10	A-11
7,12-Dimethylbenz(a)anthracene	A-1	A-3
Hexachlorophene	A-12	A-13
Hydroxydimethylarsine oxide	A-6	A-7
Malononitrile	A-14	A-15
3-Methylcholanthrene	A-1	A-4
Phenylmercury acetate	A-6	A-8
1,3-Propane sultone	A-16	A-17
2,3,7,8-Tetrachlorodibenzo-p-dioxin	A-18	A-19
Tetraethyl lead	A-20	A-21

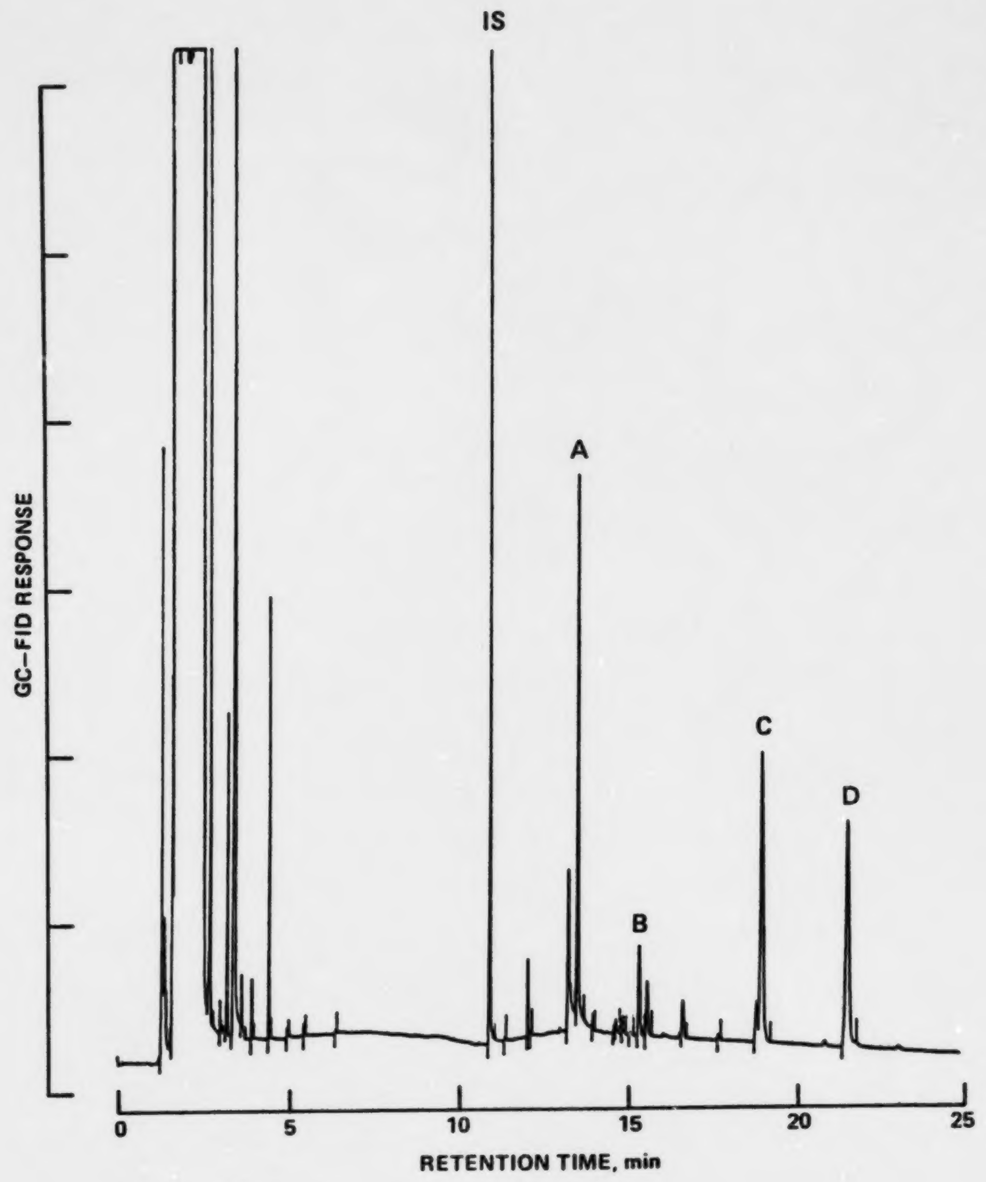

Figure A-1. Chromatogram by GC/FID for:

(A) 2-acetylaminofluorene (t_R = 13.5 min),
(B) 7,12-dimethylbenz(a)anthracene (t_R = 15.1 min),
(C) 3-methylcholanthrene (t_R = 18.6 min),
(D) dibenz(a,j)acridine (t_R = 21.5 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 20 °C/min
280 °C, 10 min isothermal

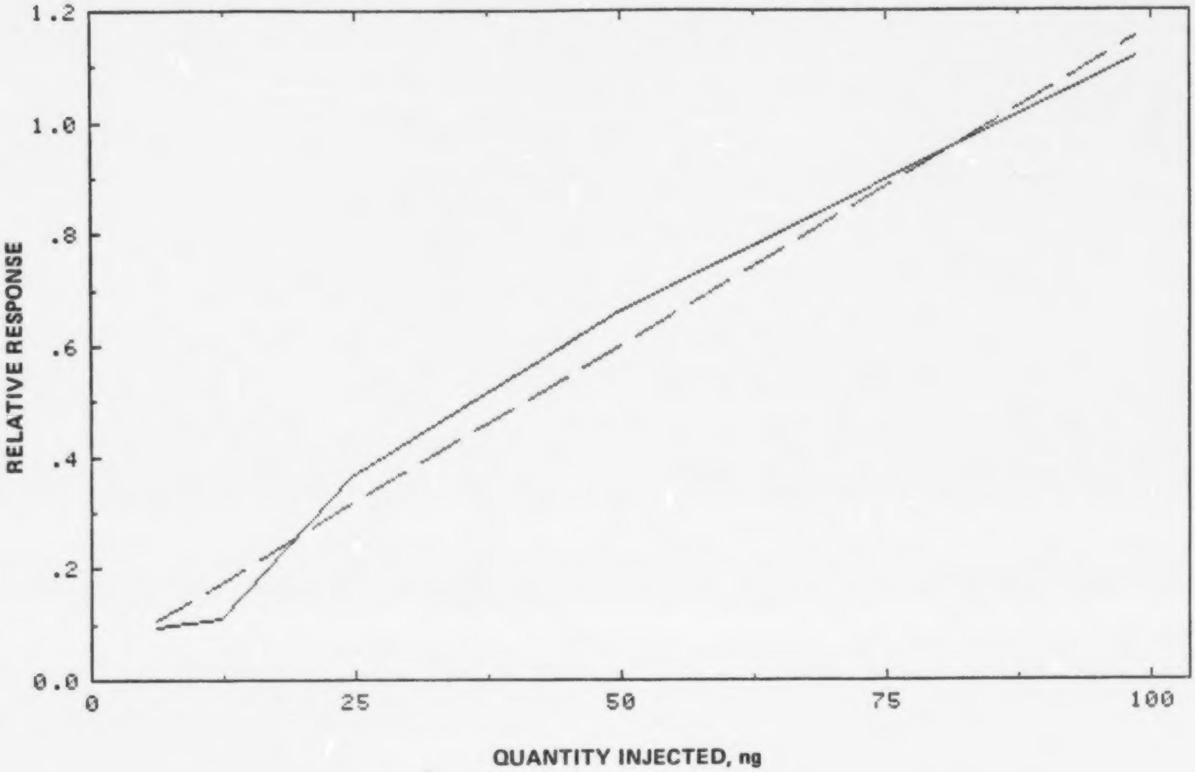

Figure A-2. Calibration curve for the determination of 2-acetylaminofluorene by GC/FID.

Range: 9-100 ng
Correlation coefficient: 0.992
Slope: 1.13×10^{-2}
y-Intercept: 3.62×10^{-2}

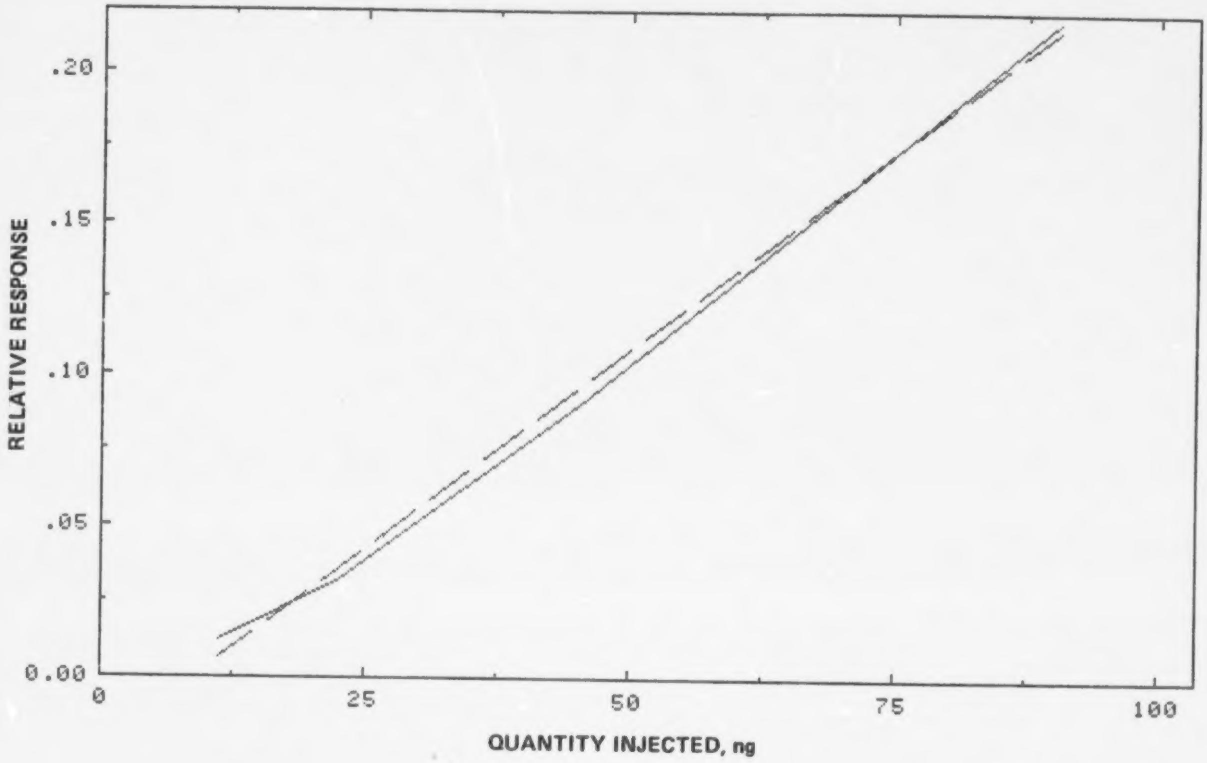

Figure A-3. Calibration curve for the determination of 7,12-dimethylbenz(a)anthracene by GC/FID.

Range: 20-100 ng
Correlation coefficient: 0.998
Slope: 2.63×10^{-3}
y-Intercept: -2.35×10^{-2}

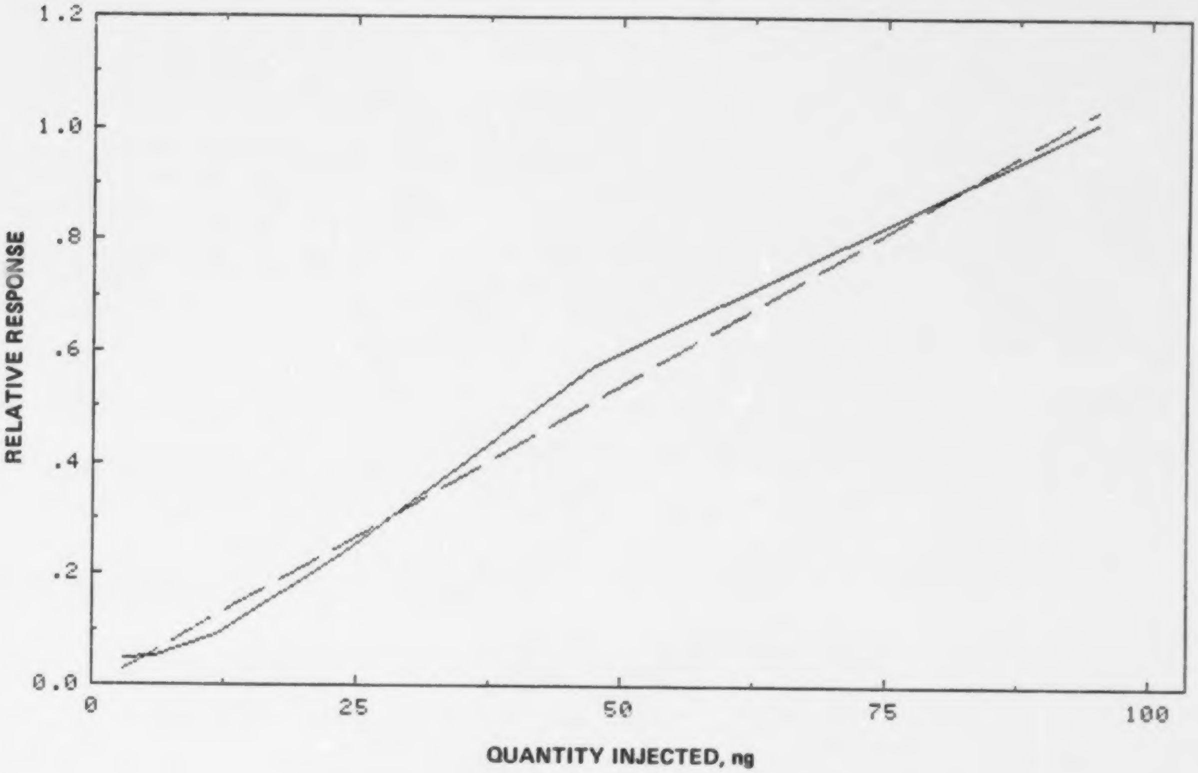

Figure A-4. Calibration curve for the determination of 3-methylcholanthrene by GC/FID.

Range: 6-100 ng
Correlation coefficient: 0.996
Slope: 1.09 x 10^{-2}
y-Intercept: -5.00 x 10^{-3}

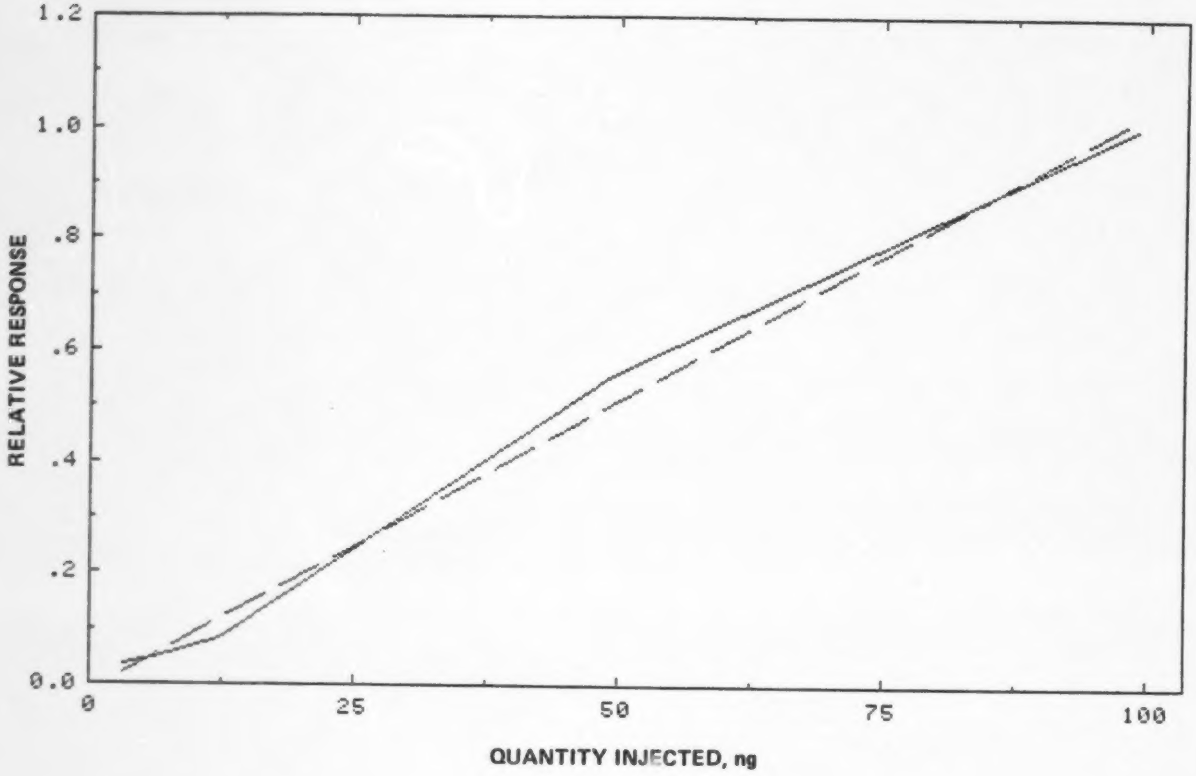

Figure A-5. Calibration curve for the determination of dibenz(a,j)acridine by GC/FID.

Range: 6-100 ng
Correlation coefficient: 0.997
Slope: 1.04×10^{-2}
y-Intercept: 1.20×10^{-2}

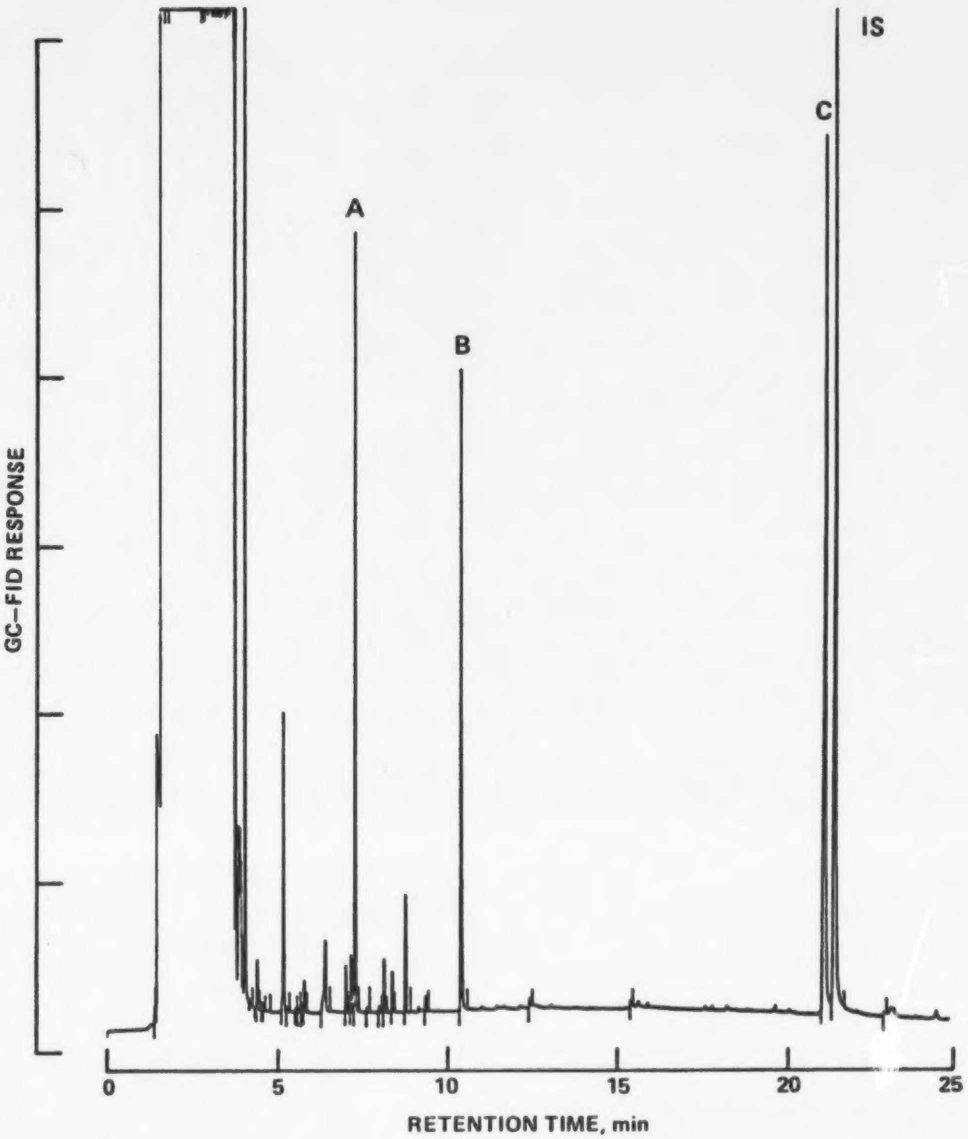

Figure A-6. Chromatogram by GC/FID for:

(A) hydroxydimethylarsine oxide (t_R = 6.6 min),
(B) phenylmercury acetate (t_R = 10.5 min),
(C) benzenearsonic acid (t_R = 21.2 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 10 min isothermal

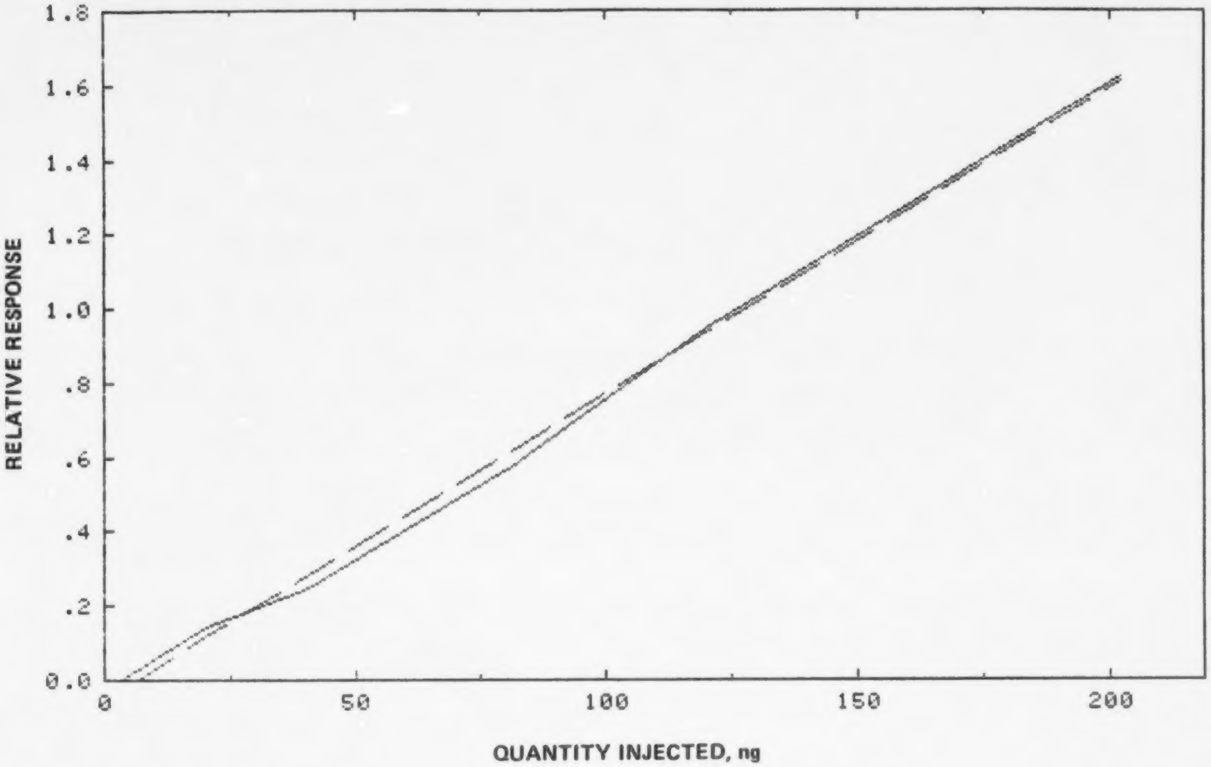

Figure A-7. Calibration curve for the determination of hydroxydimethylarsine oxide by GC/FID.

Range: 10-200 ng
Correlation coefficient: 0.999
Slope: 8.18×10^{-3}
y-Intercept: -4.96×10^{-2}

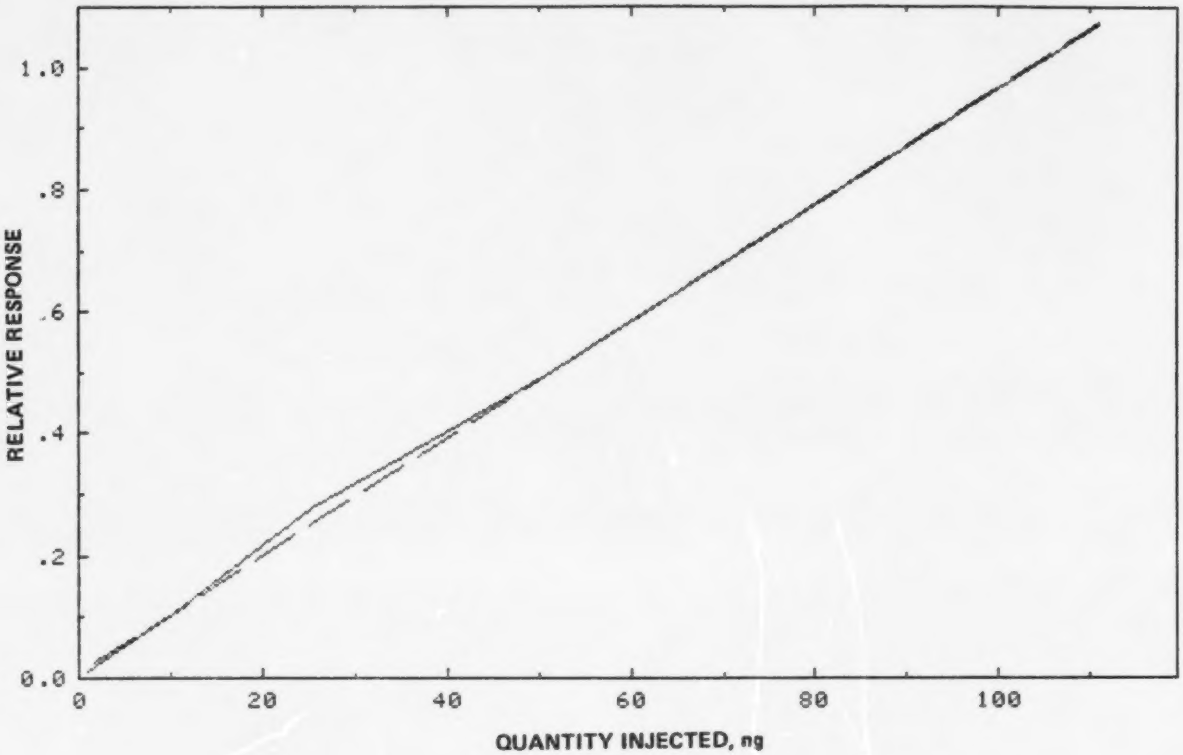

Figure A-8. Calibration curve for the determination of phenylmercury acetate by GC/FID.

Range: 1-100 ng
Correlation coefficient: 0.999
Slope: 9.64×10^{-3}
y-Intercept: 8.12×10^{-3}

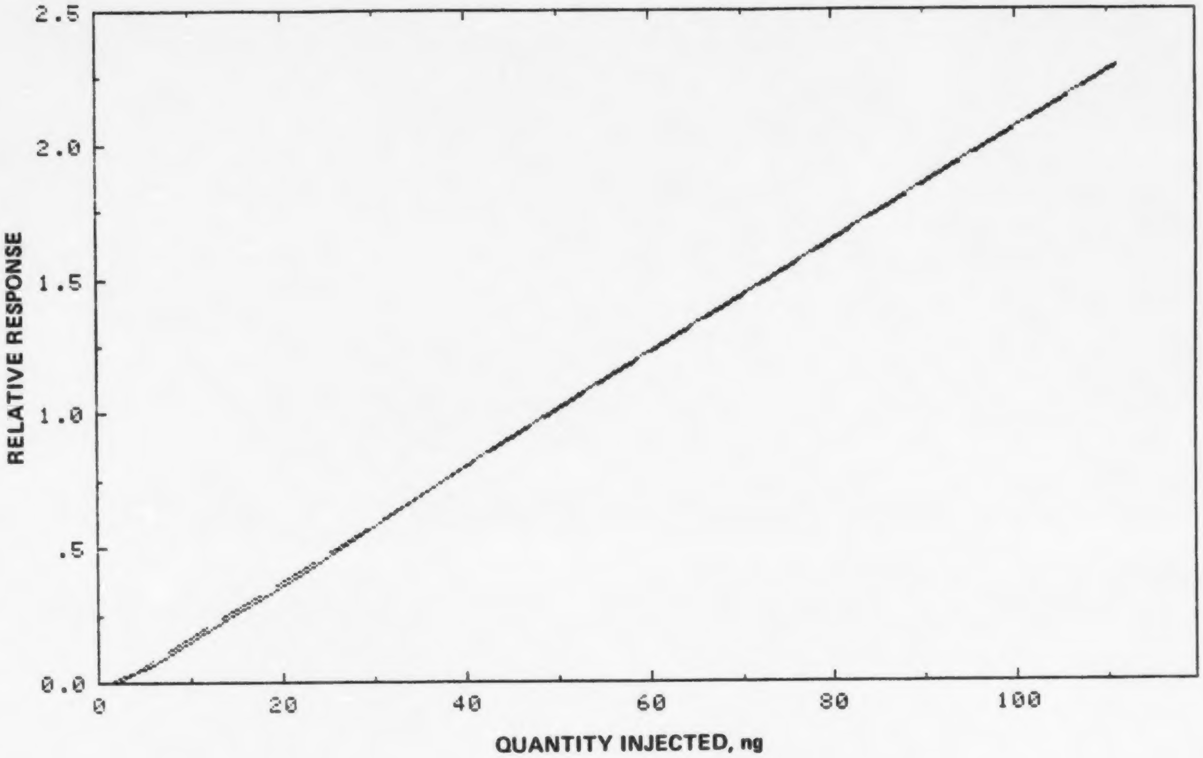

Figure A-9. Calibration curve for the determination of benzenearsonic acid by GC/FID.

Range: 2-100 ng
Correlation coefficient: 0.999
Slope: 2.11×10^{-2}
y-Intercept: -4.57×10^{-2}

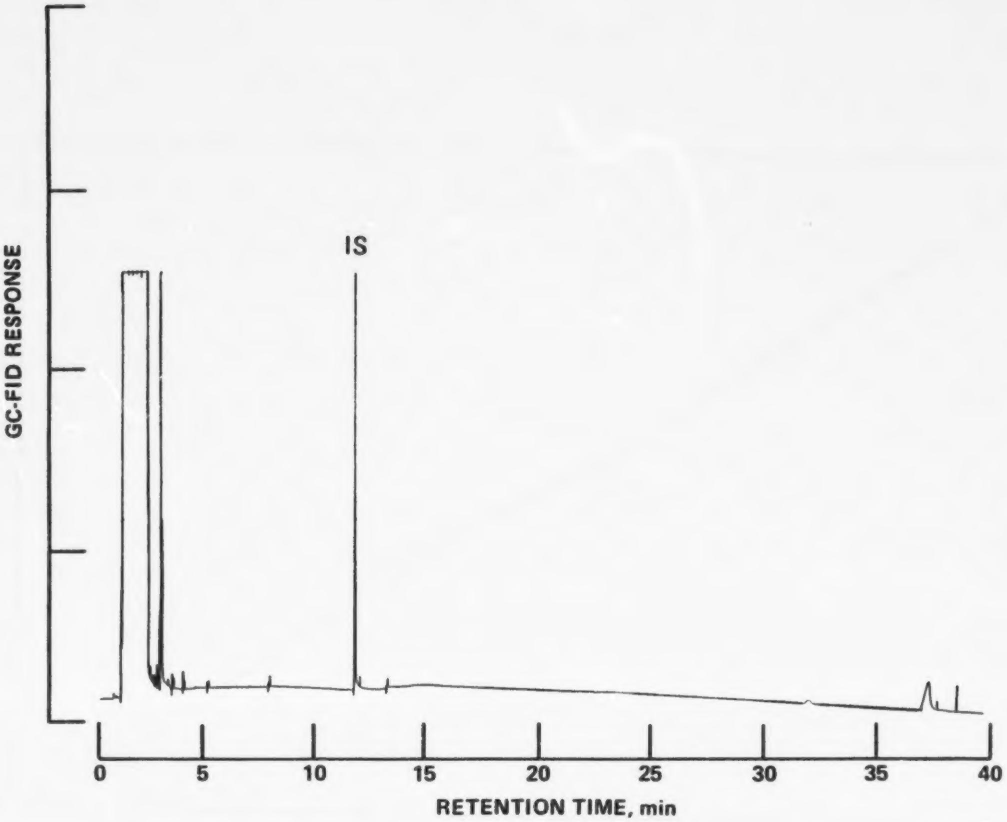

Figure A-10. Chromatogram by GC/FID for dibenzo(a,i)pyrene (t_R = 37.5 min).

Temperature program:

40 °C, 2 min isothermal
40 to 300 °C at 30 °C/min
300 °C, 10 min isothermal

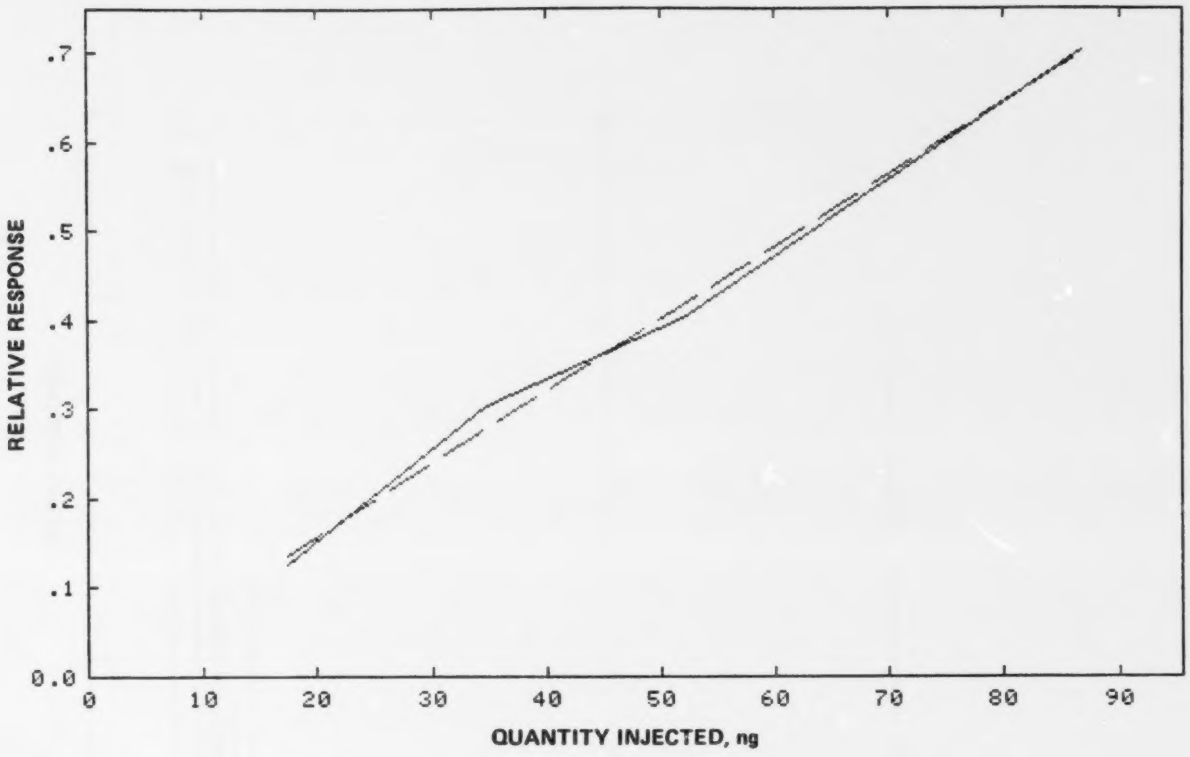

Figure A-11. Calibration curve for the determination of dibenzo(a,i)pyrene by GC/FID.

Range: 20-90 ng
Correlation coefficient: 0.997
Slope: 8.13×10^{-3}
y-Intercept: -4.86×10^{-3}

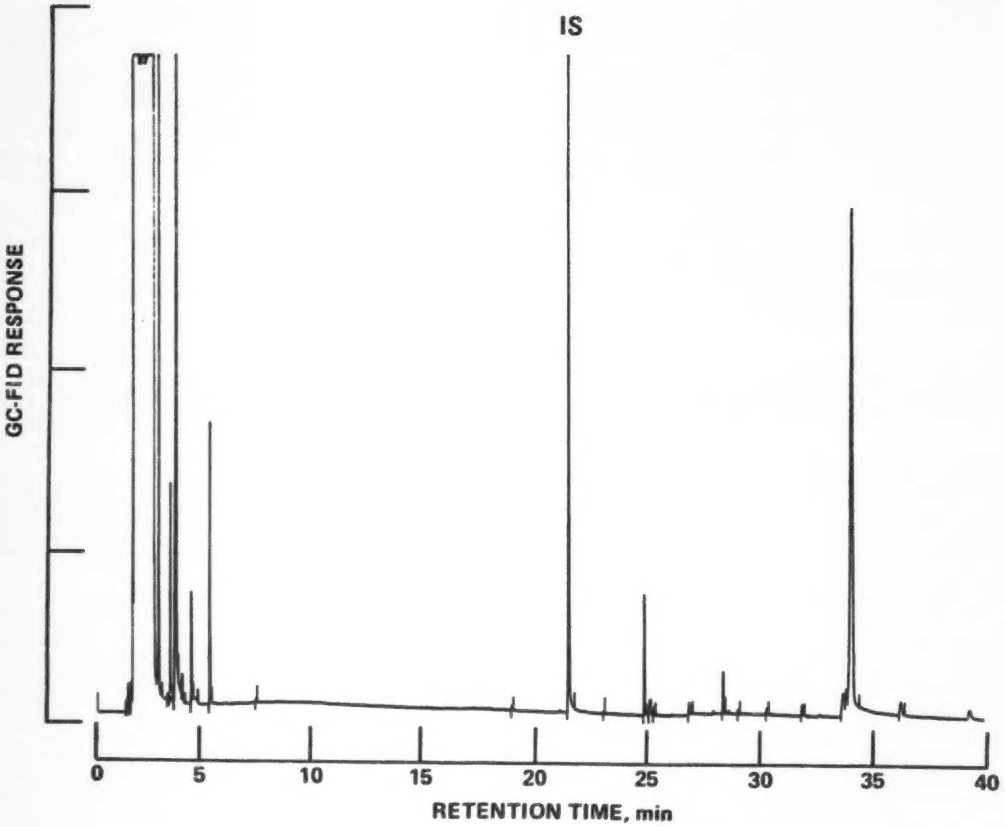

Figure A-12. Chromatogram by GC/FID for hexachlorophene (t_R = 34.0 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 10 min isothermal

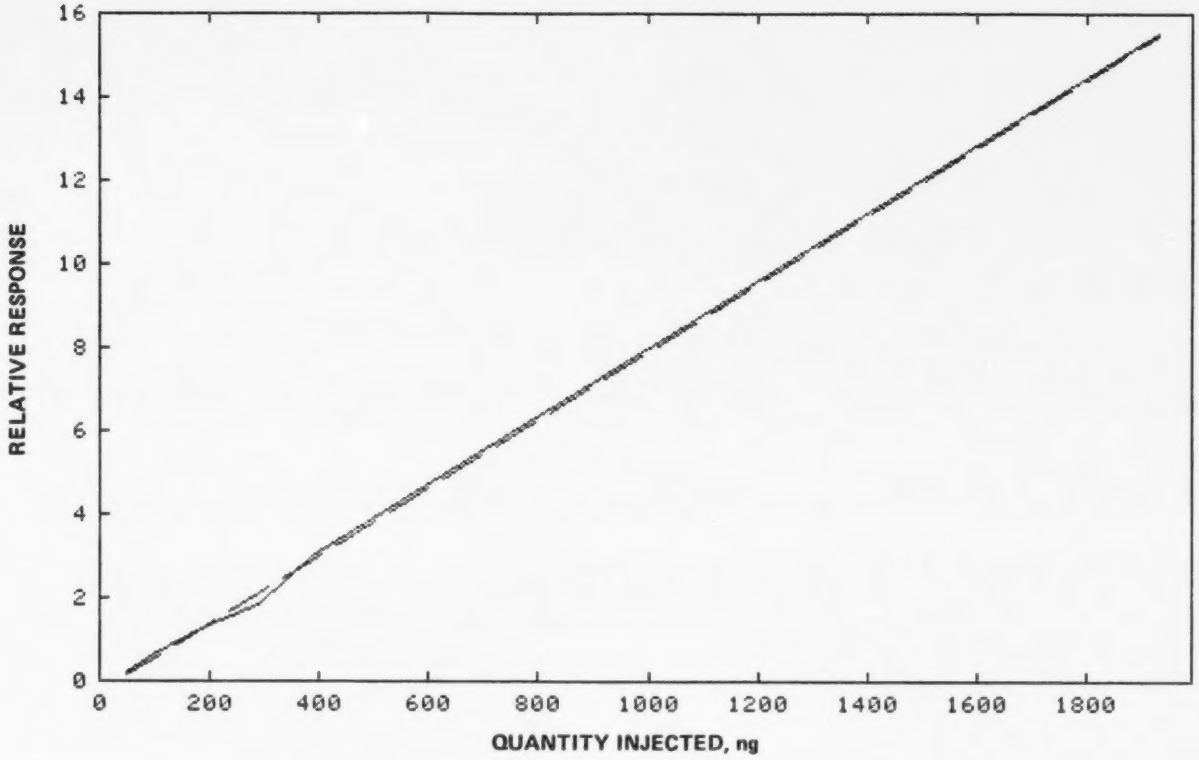

Figure A-13. Calibration curve for the determination of hexachlorophene by GC/FID.

Range: 50-2000 ng
Correlation coefficient: 0.999
Slope: 8.15×10^{-3}
y-Intercept: -2.36×10^{-1}

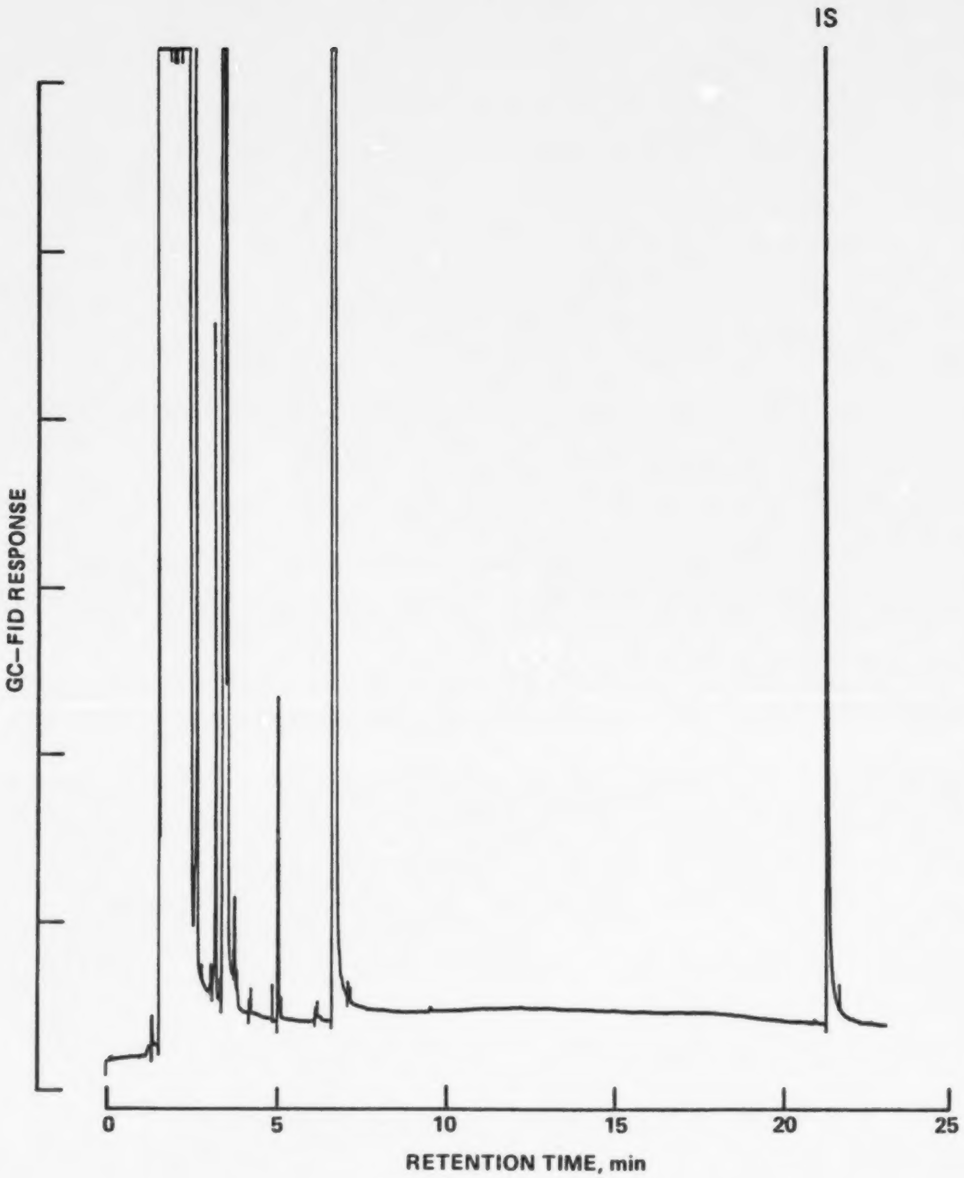

Figure A-14. Chromatogram by GC/FID for malononitrile (t_R = 6.8 min).

Temperature program:

40 °C, 3 min isothermal
40 to 300 °C at 10 °C/min
300 °C, 10 min isothermal

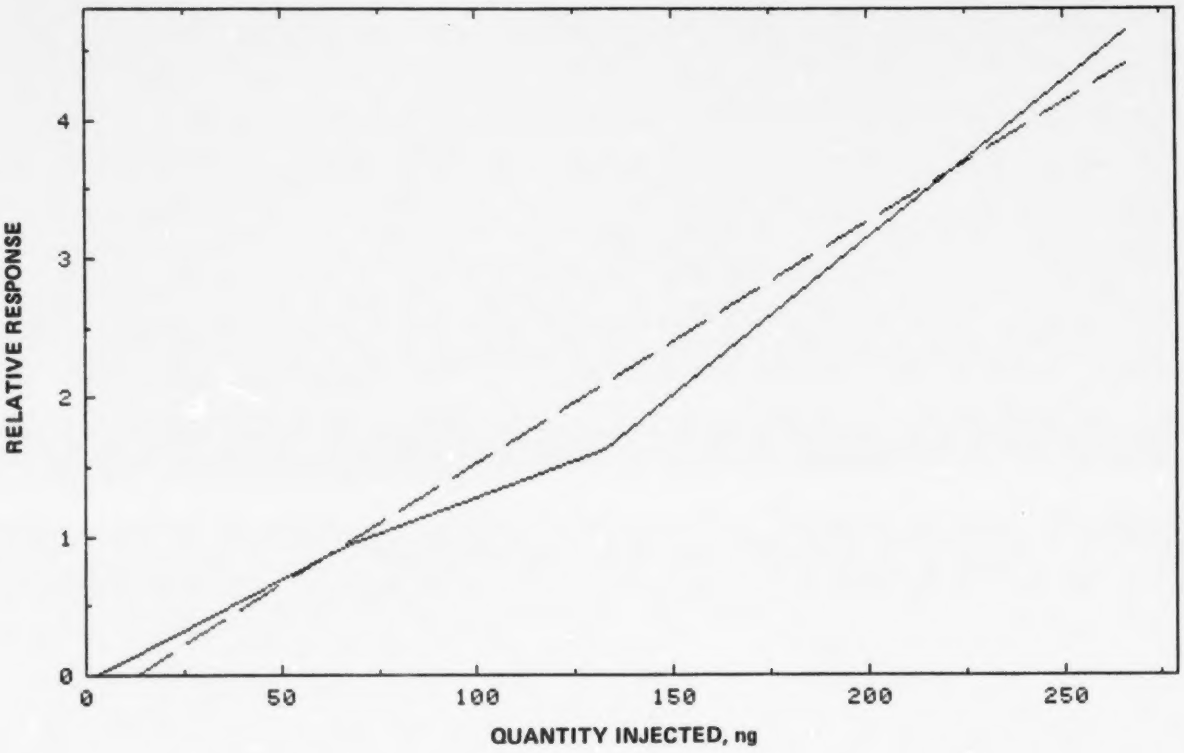

Figure A-15. Calibration curve for the determination of malononitrile by GC/FID.

Range: 20-250 ng
Correlation coefficient: 0.989
Slope: 1.73 x 10^{-2}
y-Intercept: -2.06 x 10^{-1}

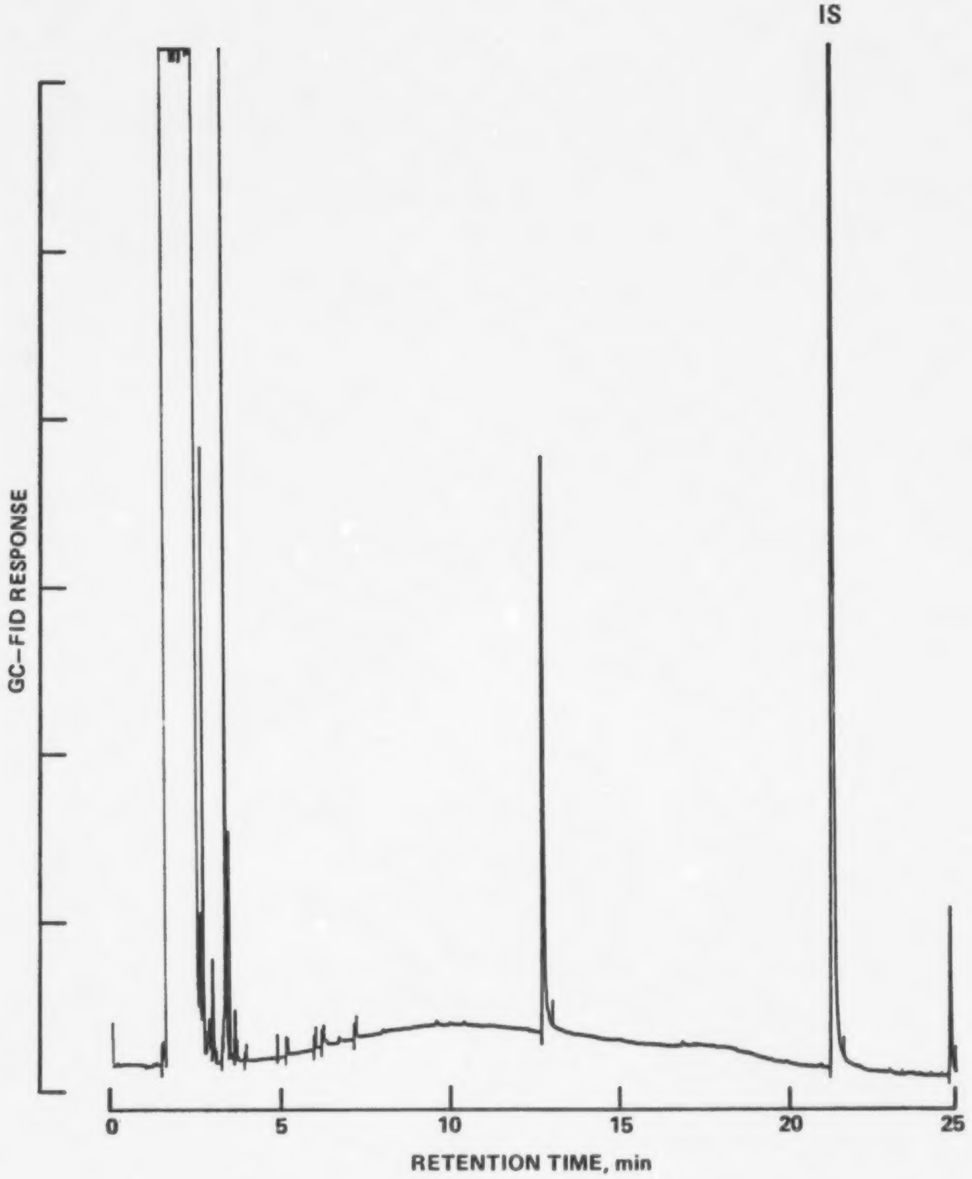

Figure A-16. Chromatogram by GC/FID for 1,3-propane sultone (t_R = 12.7 min).

Temperature program:

40 °C, 3 min isothermal
40 to 300 °C at 10 °C/min
300 °C, 10 min isothermal

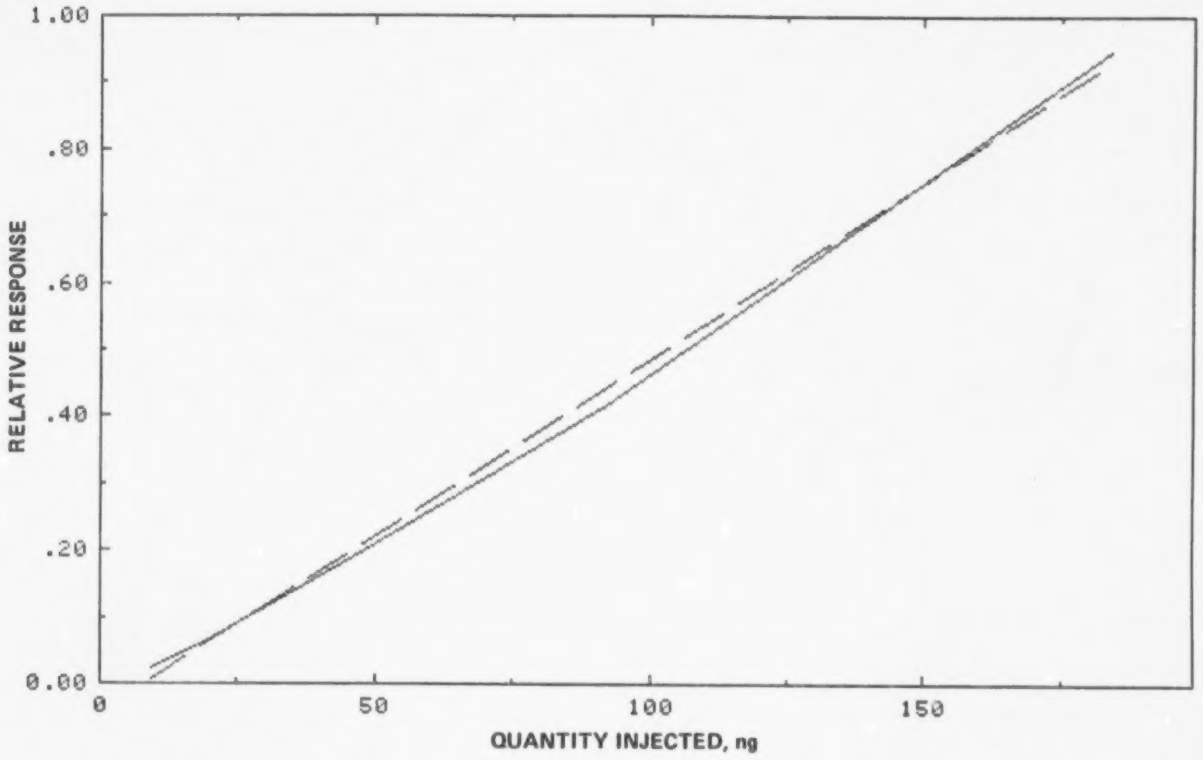

Figure A-17. Calibration curve for the determination of 1,3-propane sultone by GC/FID.

Range: 5-180 ng
Correlation coefficient: 0.999
Slope: 5.30×10^{-3}
y-Intercept: -4.29×10^{-2}

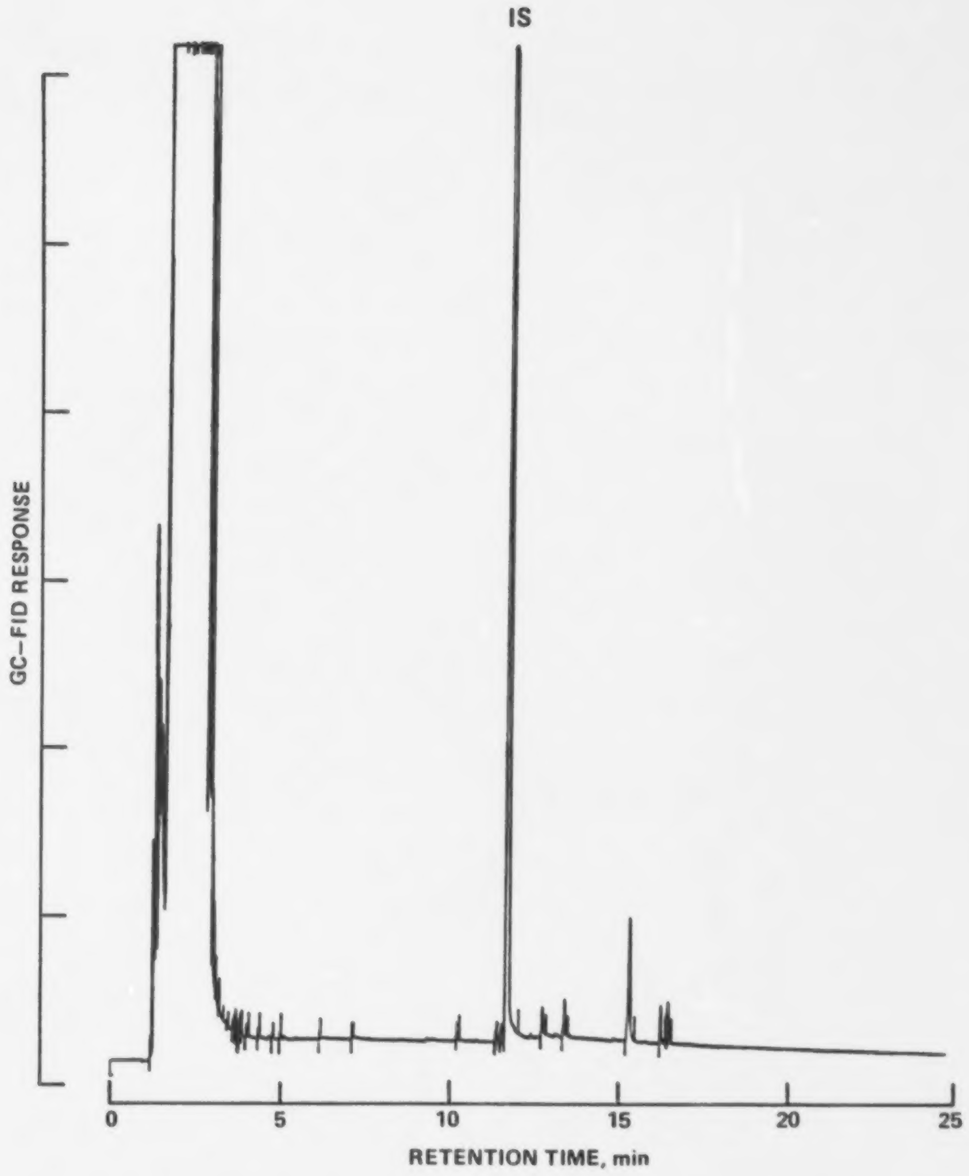

Figure A-18. Chromatogram by GC/FID for 2,3,7,8-tetrachlorodibenzo-p-dioxin (t_R = 15.2 min).

Temperature program:

60 °C, 4 min isothermal
60 to 300 °C at 20 °C/min
300 °C, 10 min isothermal

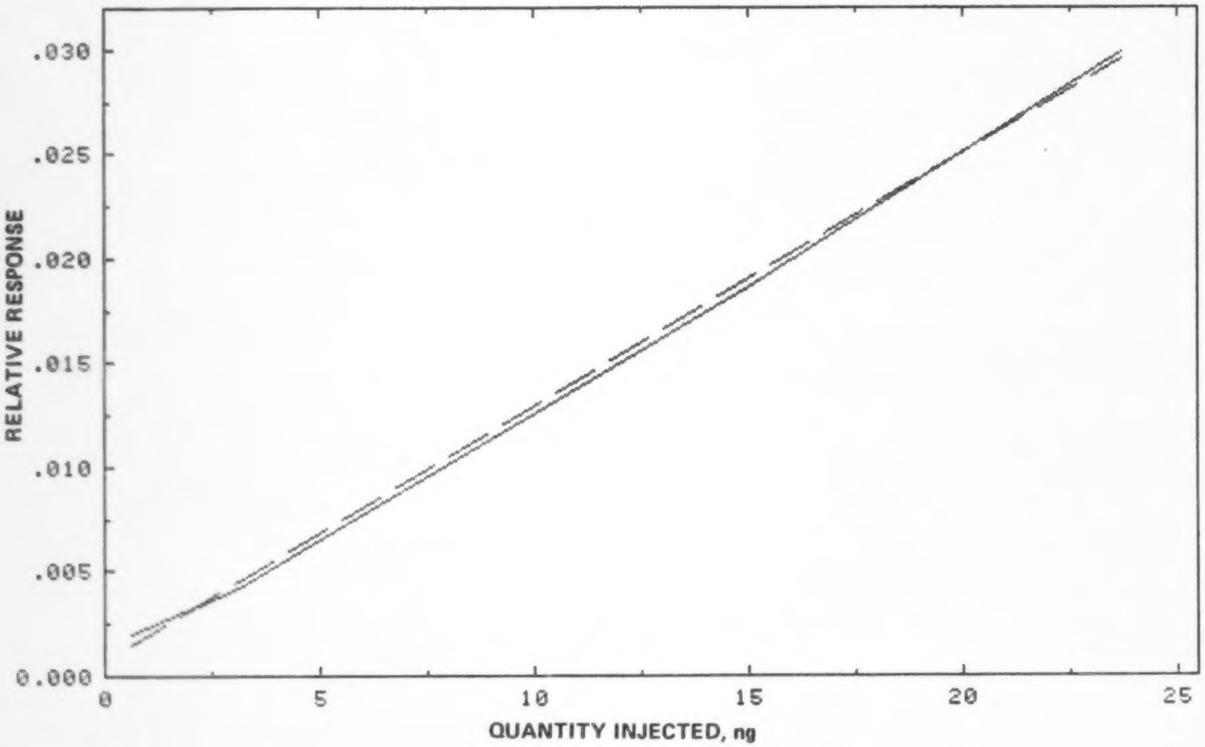

Figure A-19. Calibration curve for the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin by GC/FID.

Range: 0.7-25 ng
Correlation coefficient: 0.950
Slope: 3.74×10^{-3}
y-Intercept: 2.10×10^{-4}

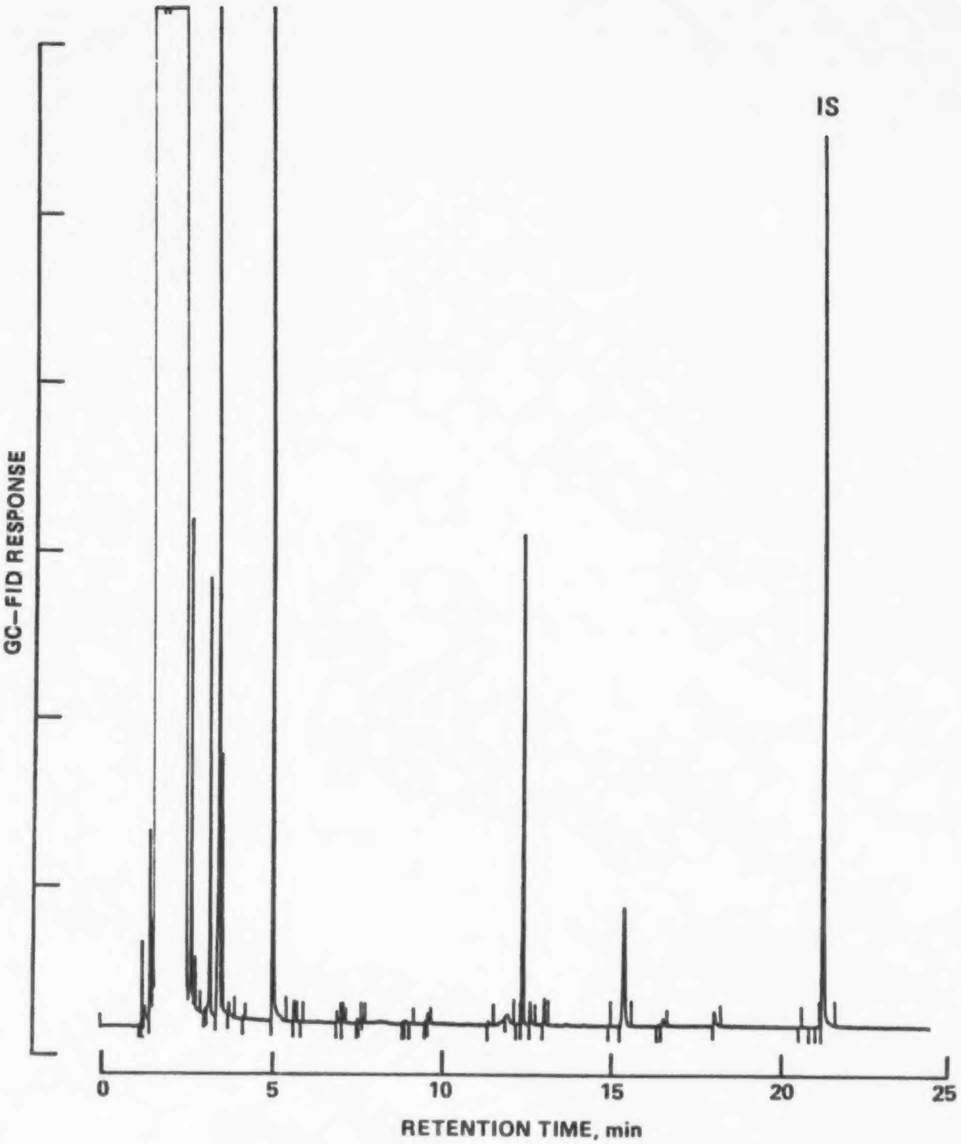

Figure A-20. Chromatogram by GC/FID for tetraethyl lead (t_R = 12.4 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 10 min isothermal

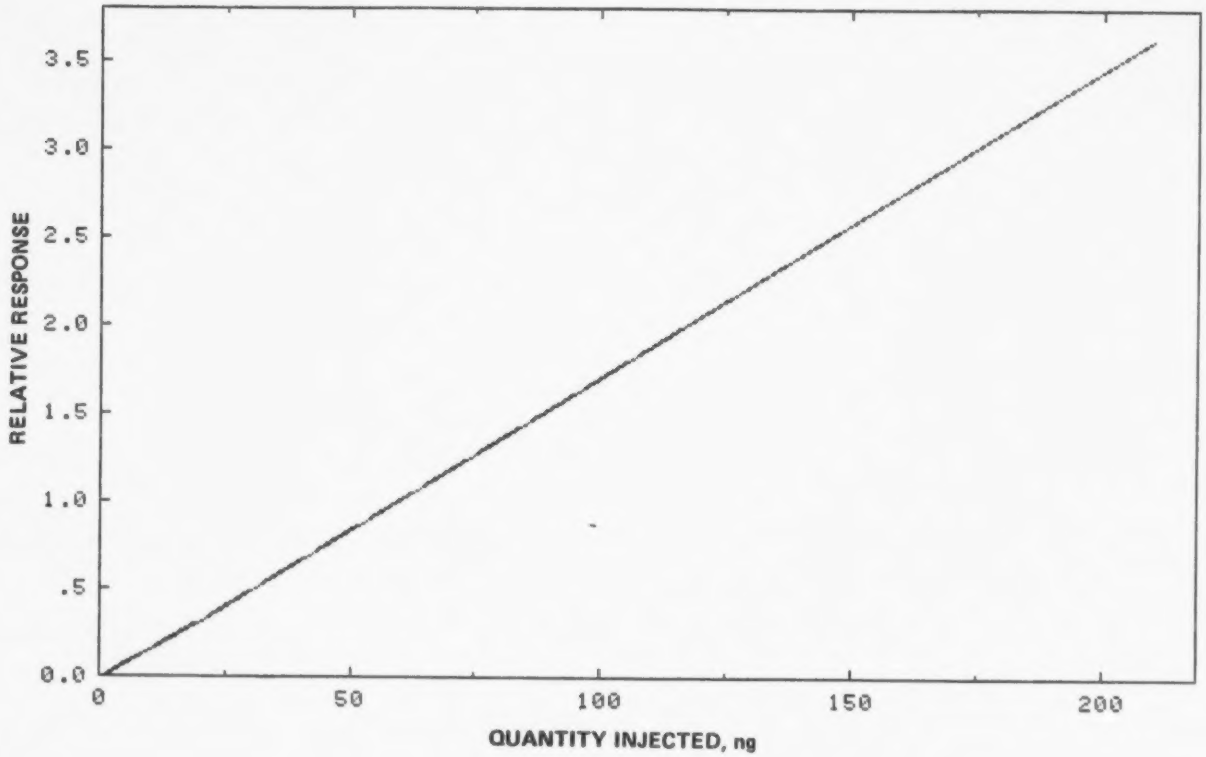

Figure A-21. Calibration curve for the determination of tetraethyl lead by GC/FID.

Range: 0.7-200 ng
Correlation coefficient: 0.999
Slope: 1.74×10^{-2}
y-Intercept: -2.26×10^{-2}

APPENDIX B

CHROMATOGRAMS, MASS SPECTRA, AND CALIBRATION CURVES FOR GC/MS DETERMINATIONS

Index

Compound	Reference chromatogram Figure No.	Reference mass spectrum Figure No.	Reference calibration curve Figure No.
2-Acetylaminofluorene	B-1	B-2	B-3
Benzenearsonic acid	B-10	B-11	B-12
Dibenz(a,j)acridine	B-1	B-8	B-9
Dibenzo(a,i)pyrene	B-13	B-14	B-15
7,12-Dimethylbenz(a)anthracene	B-1	B-4	B-5
Hexachlorophene	B-16	B-17	B-18
Hydroxydimethylarsine oxide	B-19	B-20	B-21
Malononitrile	B-22	B-23	B-24
3-Methylcholanthrene	B-1	B-6	B-7
Phenylmercury acetate	B-25	B-26	B-27
1,3-Propane sultone	B-28	B-29	B-30
2,3,7,8-Tetrachlorodibenzo-_p_-dioxin	B-31	B-32	B-33
Tetraethyl lead	B-34	B-35	B-36

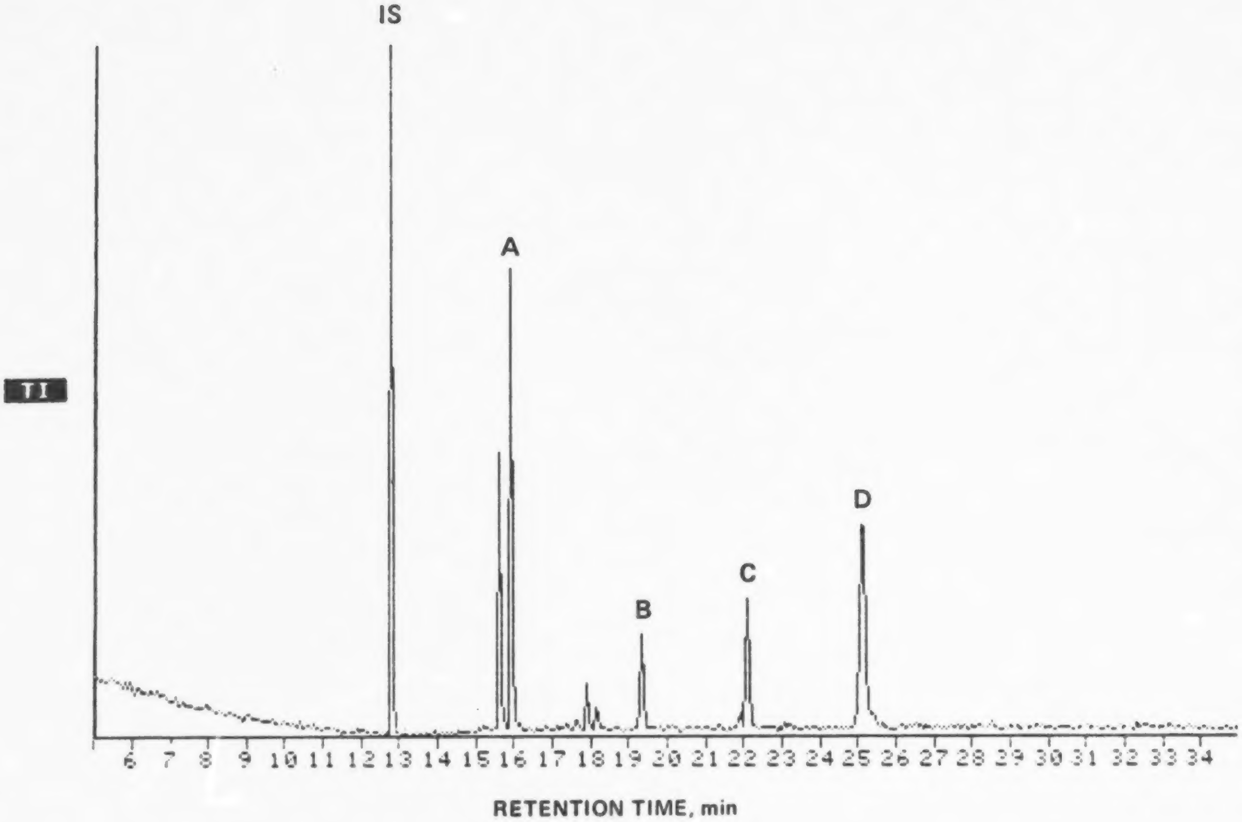

Figure B-1. Chromatogram by GC/MS for:

(A) 2-acetylaminofluorene (t_R = 16.0 min),
(B) 7,12-dimethylbenz(a)anthracene (t_R = 19.5 min),
(C) 3-methylcholanthrene (t_R = 22.2 min),
(D) dibenz(a,j)acridine (t_R = 25.3 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 20 °C/min
280 °C, 10 min isothermal

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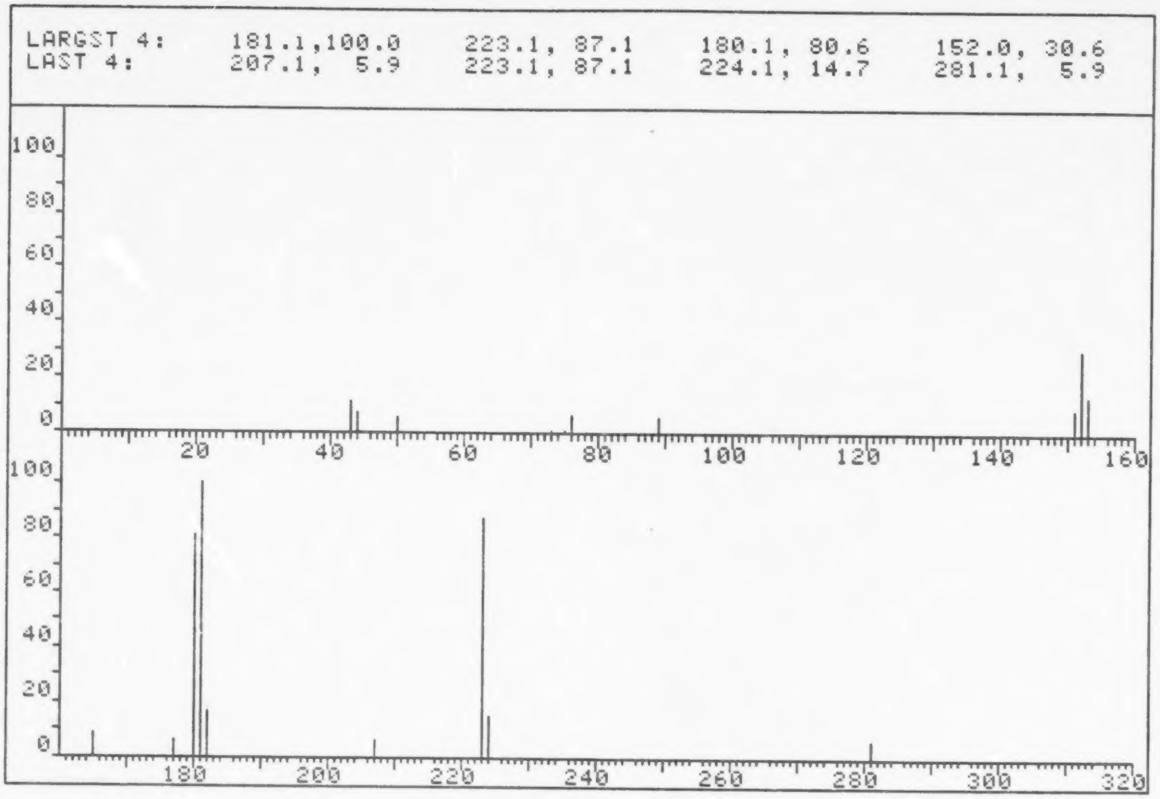


```
LARGST 4:   181.1,100.0   223.1, 87.1   180.1, 80.6   152.0, 30.6
LAST 4:     207.1,  5.9   223.1, 87.1   224.1, 14.7   281.1,  5.9
```

Figure B-2. Mass spectrum for 2-acetylaminofluorene.

TABLE B-1. KEY IONS AND RELATIVE ABUNDANCES FOR 2-ACETYLAMINOFLUORENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43	6.4	126	2.7	154	2.2	180	79.0
63	2.8	127	3.7	163	4.6	181	100.0
74	2.3	150	3.4	164	3.1	182	17.1
75	3.8	151	10.4	165	6.0	223	72.6
76	3.5	152	26.2	177	2.1	224	14.6
77	2.3	153	13.2	178	3.1		

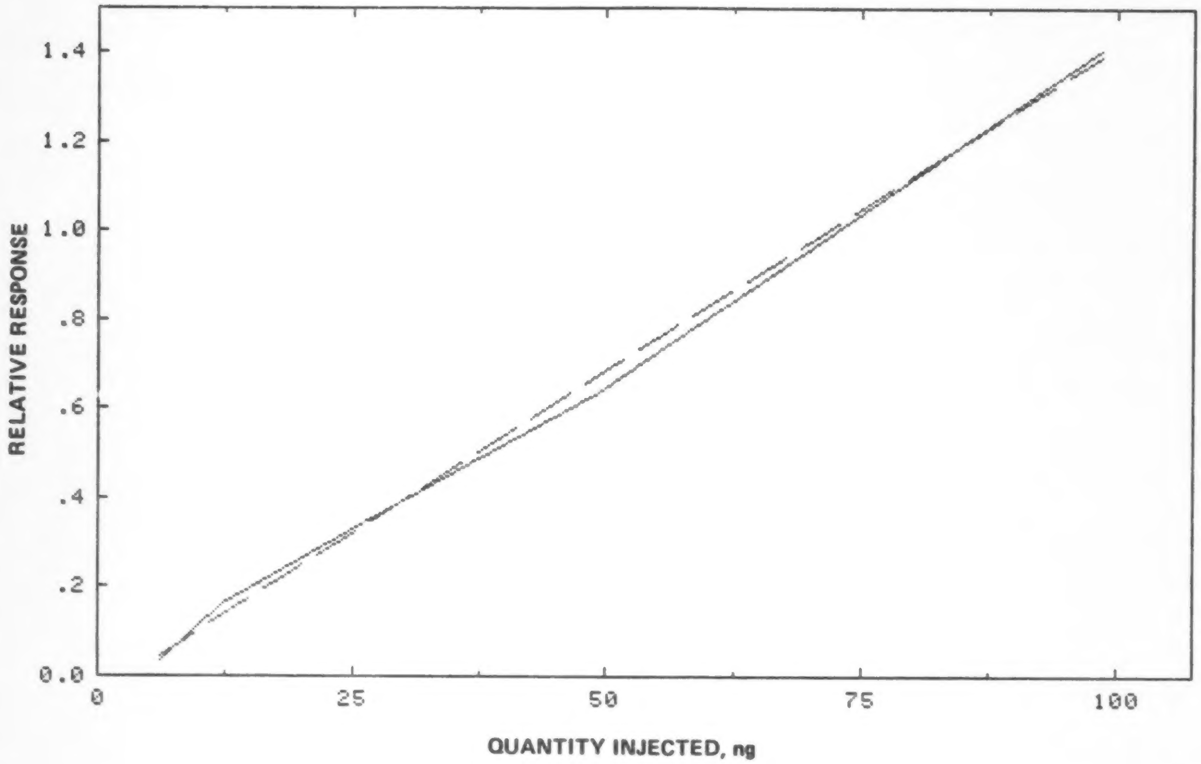
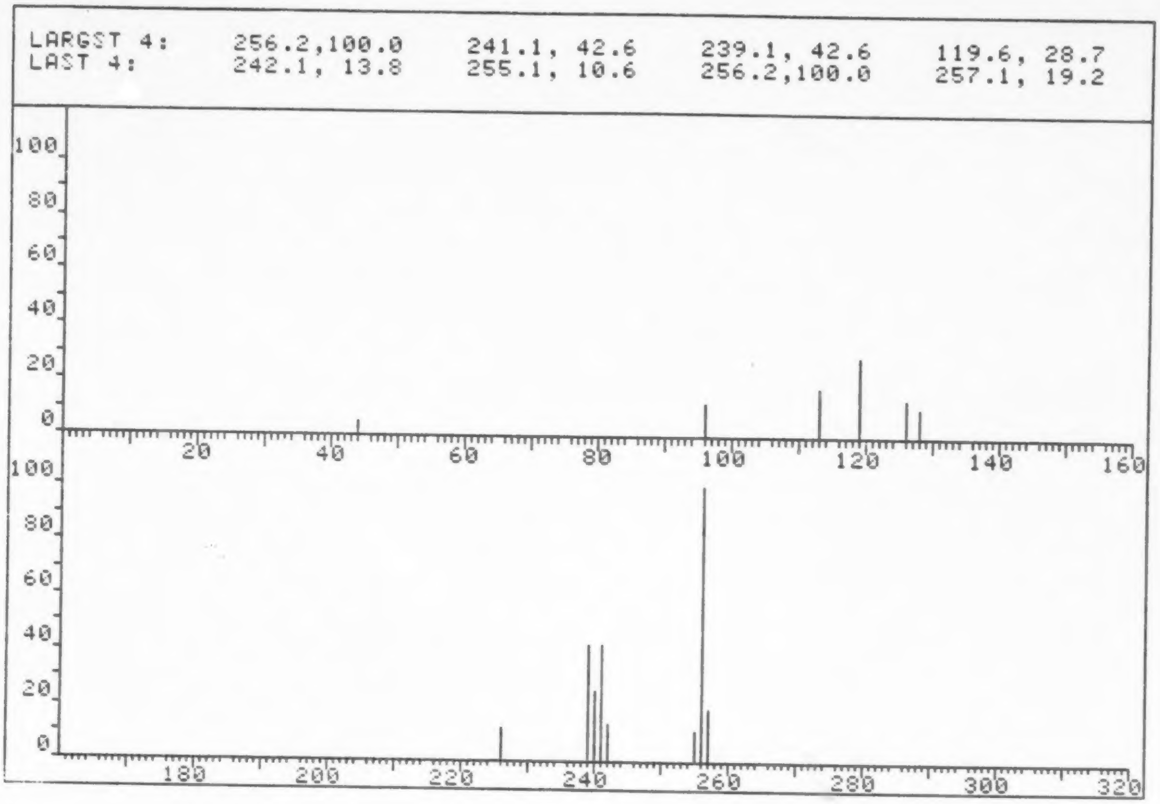


Figure B-3. Calibration curve for the determination of 2-acetylaminofluorene by GC/MS.

Range: 6-100 ng
Correlation coefficient: 0.999
Slope: 1.46×10^{-2}
y-Intercept: -4.374×10^{-2}



```
LARGST 4:     256.2,100.0     241.1, 42.6     239.1, 42.6     119.6, 28.7
LAST 4:       242.1, 13.8     255.1, 10.6     256.2,100.0     257.1, 19.2
```

Figure B-4. Mass spectrum for 7,12-dimethylbenz(a)anthracene.

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TABLE B-2. KEY IONS AND RELATIVE ABUNDANCES FOR 7,12-DIMETHYLBENZ(a)ANTHRACENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
44	5.9	112	7.4	128	11.4	250	9.4
46	4.9	113	13.9	226	7.9	252	10.4
53	5.9	120	31.7	239	40.6	253	7.4
100	5.4	125	7.9	240	29.2	255	12.9
101	6.9	126	13.9	241	45.5	256	100.0
106	4.9	127	8.4	242	10.4	257	18.3

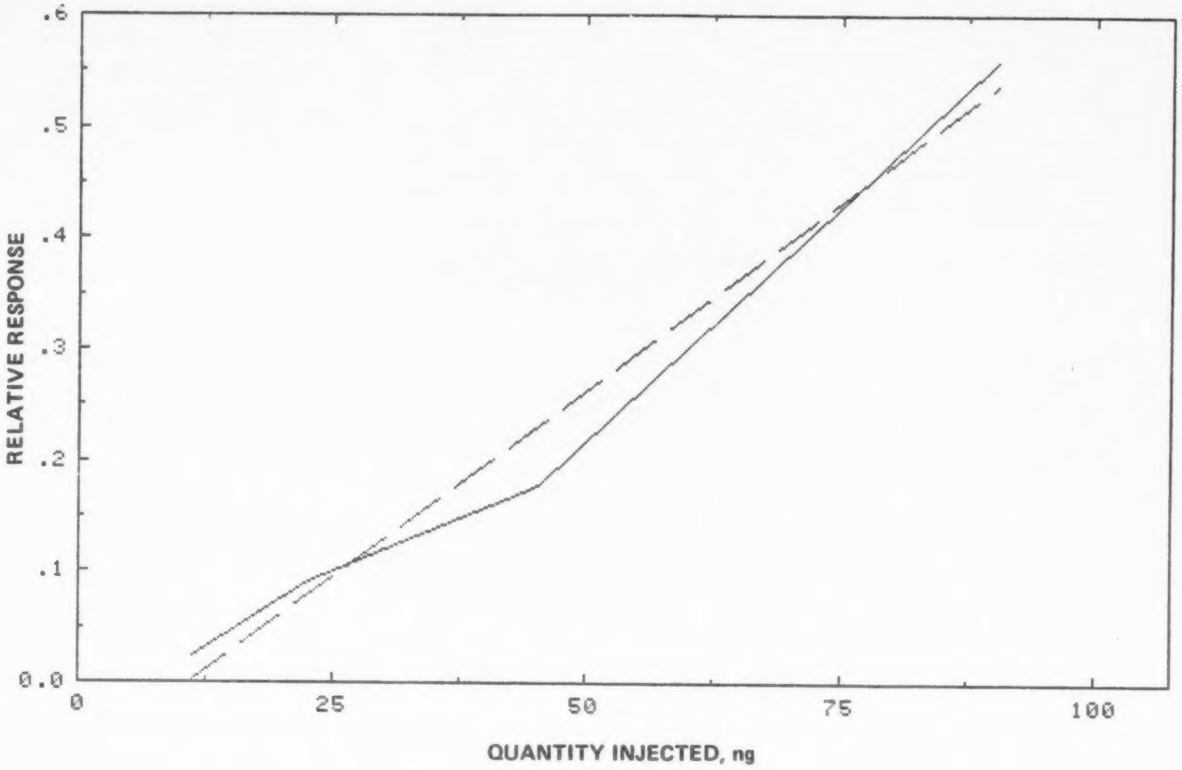
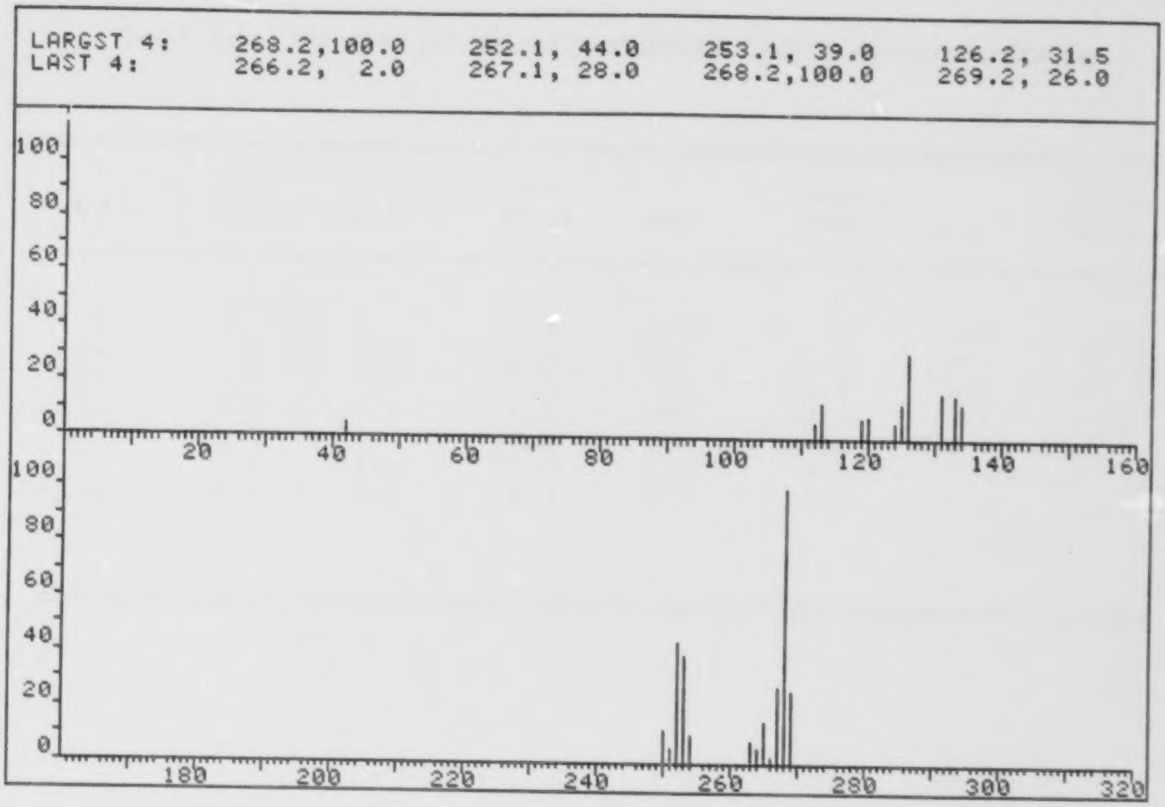


Figure B-5. Calibration curve for the determination of 7,12-dimethylbenz(a)anthracene by GC/MS.

Range: 10-100 ng
Correlation coefficient: 0.988
Slope: 6.76×10^{-3}
y-Intercept: -7.43×10^{-2}



```
LARGST 4:     268.2,100.0     252.1, 44.0     253.1, 39.0     126.2, 31.5
LAST 4:       266.2,  2.0     267.1, 28.0     268.2,100.0     269.2, 26.0
```

Figure B-6. Mass spectrum for 3-methylcholanthrene.

TABLE B-3. KEY IONS AND RELATIVE ABUNDANCES FOR 3-METHYLCHOLANTHRENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
75	6.1	119	18.9	239	8.5	266	3.7
94	7.9	125	20.7	250	11.6	267	25.6
106	6.1	126	65.2	252	48.8	268	100.0
112	9.8	130	14.6	253	38.4	269	20.7
113	19.5	131	30.5	254	9.1		
117	7.3	133	28.7	263	9.8		
118	15.2	134	24.4	265	13.4		

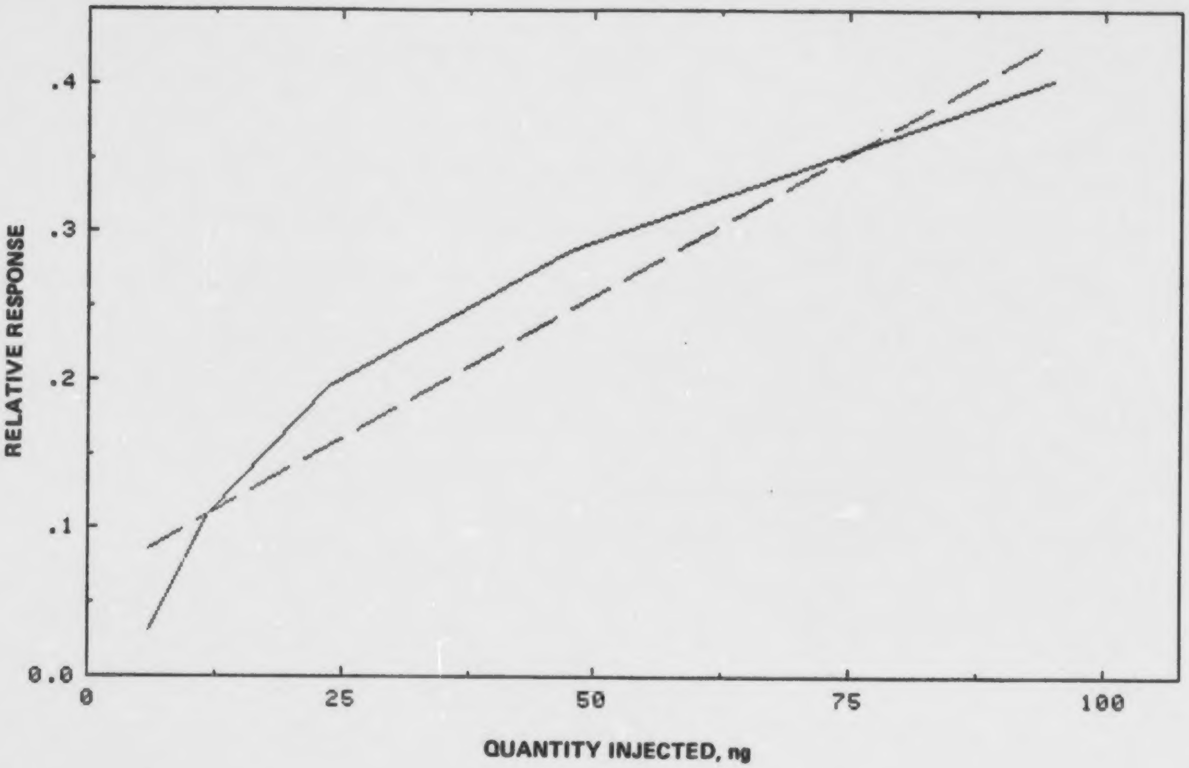
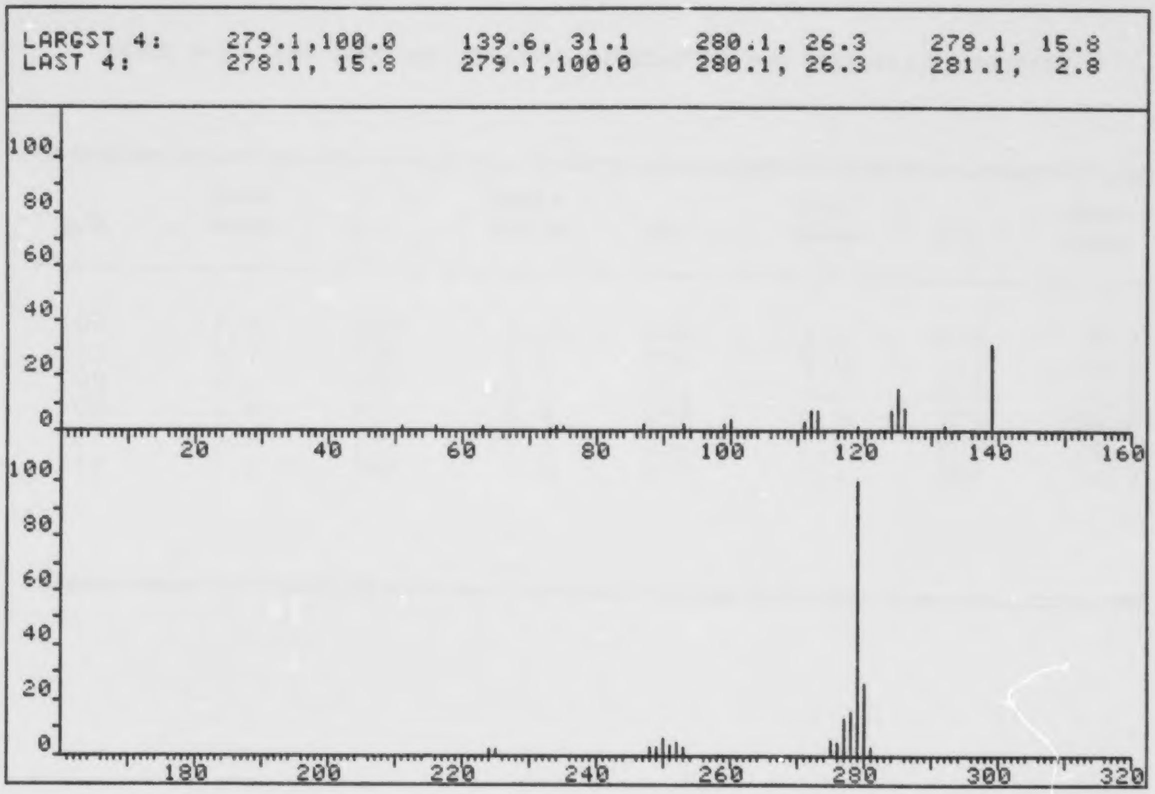


Figure B-7. Calibration curve for the determination of 3-methylcholanthrene by GC/MS.

Range: 10-100 ng
Correlation coefficient: 0.957
Slope: 3.86×10^{-3}
y-Intercept: 6.34×10^{-2}



```
LARGST 4:    279.1,100.0    139.6, 31.1    280.1, 26.3    278.1, 15.8
LAST 4:      278.1, 15.8    279.1,100.0    280.1, 26.3    281.1,  2.8
```

Figure B-8. Mass spectrum for dibenz(a,j)acridine.

TABLE B-4. KEY IONS AND RELATIVE ABUNDANCES FOR DIBENZ(a,j)ACRIDINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
87	2.5	113	7.4	249	3.1	276	4.4
93	2.1	124	7.4	250	5.9	277	13.2
99	2.6	125	15.2	251	4.0	278	15.8
100	4.0	126	8.4	252	4.3	279	100.0
111	3.6	139	31.1	253	2.8	280	26.4
112	7.6	248	2.5	275	5.4	281	4.4

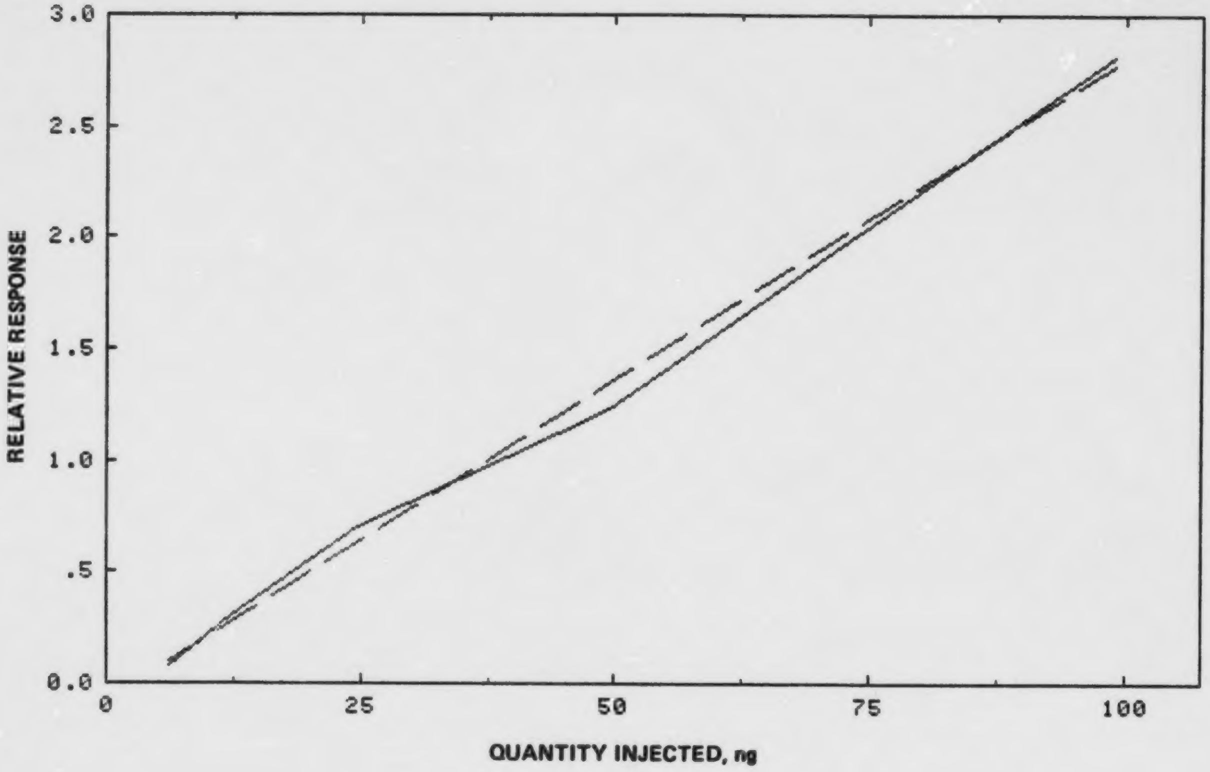


Figure B-9. Calibration curve for the determination of dibenz(a,j)acridine by GC/MS.

Range: 6-100 ng
Correlation coefficient: 0.998
Slope: 2.89×10^{-2}
y-Intercept: -8.08×10^{-2}

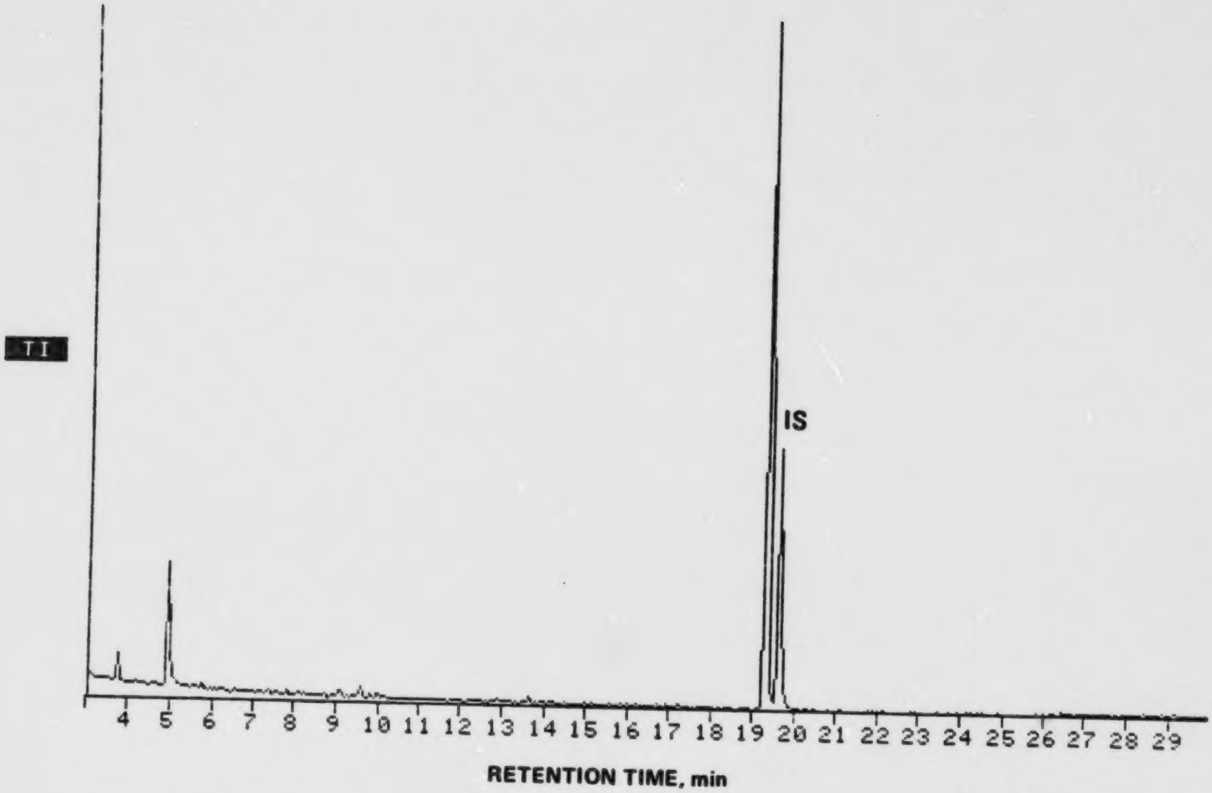


Figure B-10. Chromatogram by GC/MS for benzenearsonic acid (t_R = 19.3 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 10 min isothermal

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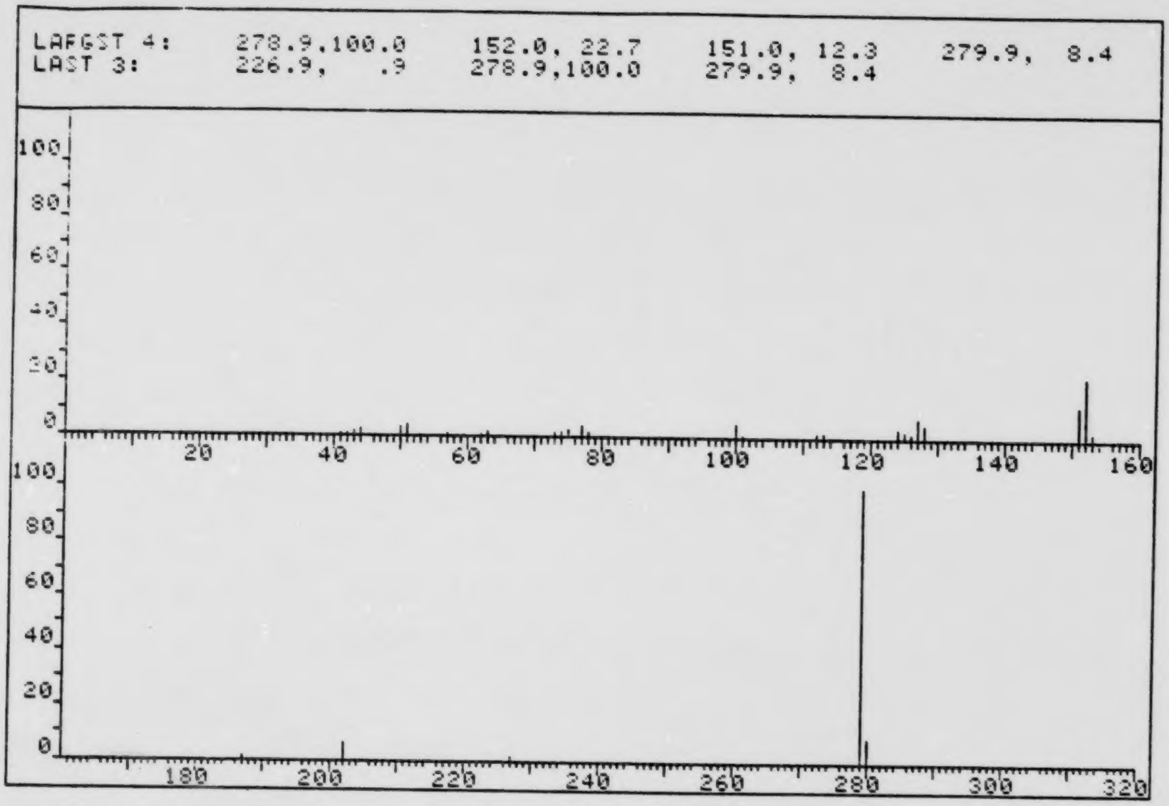


```
LARGST 4:    278.9,100.0    152.0, 22.7    151.0, 12.3    279.9,  8.4
LAST 3:      226.9,    .9   278.9,100.0    279.9,  8.4
```

Figure B-11. Mass spectrum for benzenearsonic acid.

TABLE B-5. KEY IONS AND RELATIVE ABUNDANCES FOR BENZENEARSONIC ACID

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.0	.9	74.9	2.3	127.9	5.2
42.1	1.0	77.1	4.0	151.0	12.3
43.0	1.3	78.0	1.6	152.0	22.7
44.0	2.2	100.0	5.2	153.0	2.3
50.0	2.9	101.0	1.2	186.9	1.3
51.0	4.4	111.9	1.4	201.9	6.2
57.1	.9	112.9	1.4	226.9	.9
62.3	1.2	124.0	3.0	278.9	100.0
63.2	1.6	124.9	2.1	279.9	8.4
73.1	1.3	126.0	1.7	328.7	2.6
74.0	1.6	126.9	7.3		

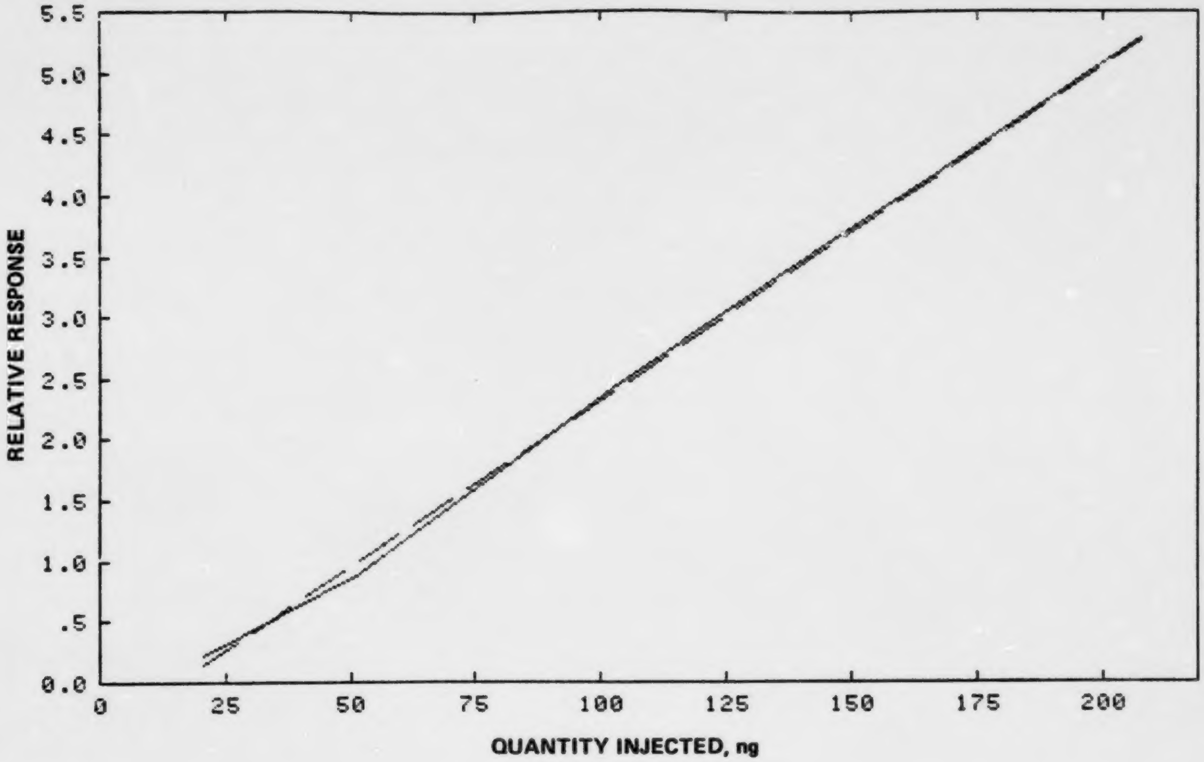


Figure B-12. Calibration curve for the determination of benzenearsonic acid by GC/MS.

Range: 20-200 ng
Correlation coefficient: 0.999
Slope: 2.74×10^{-2}
y-Intercept: -4.28×10^{-1}

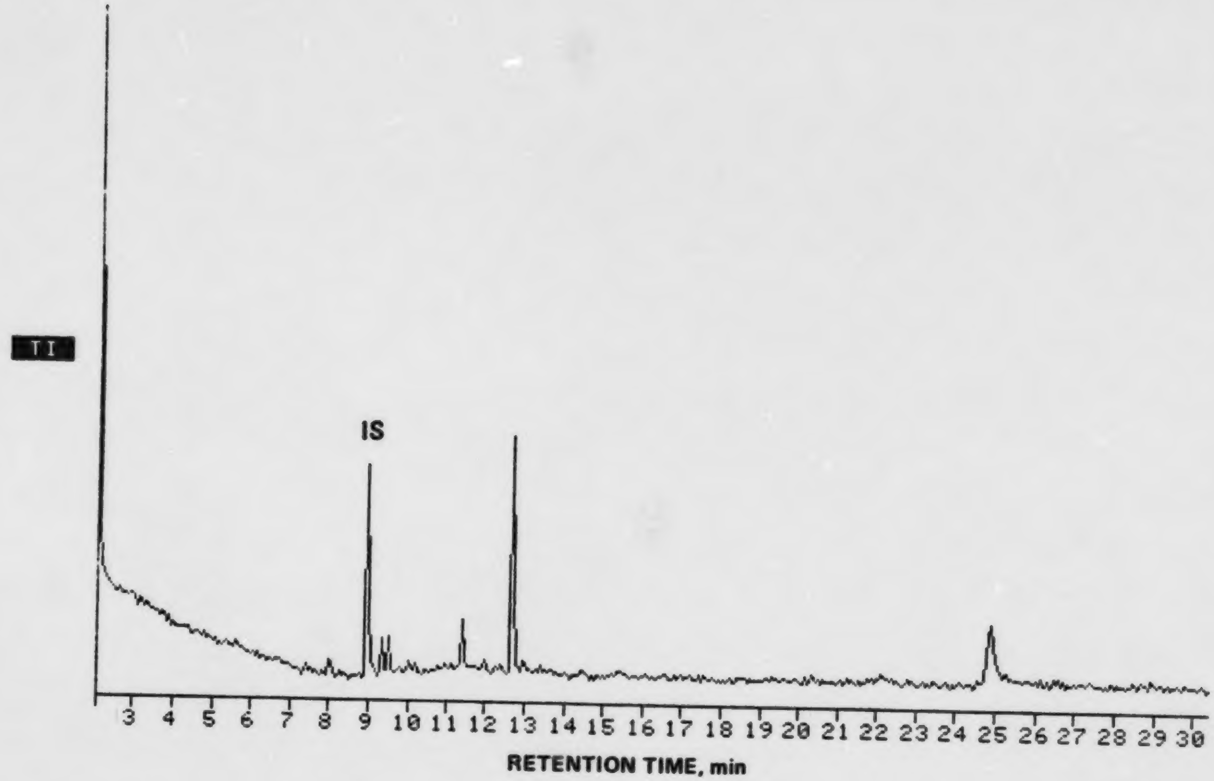
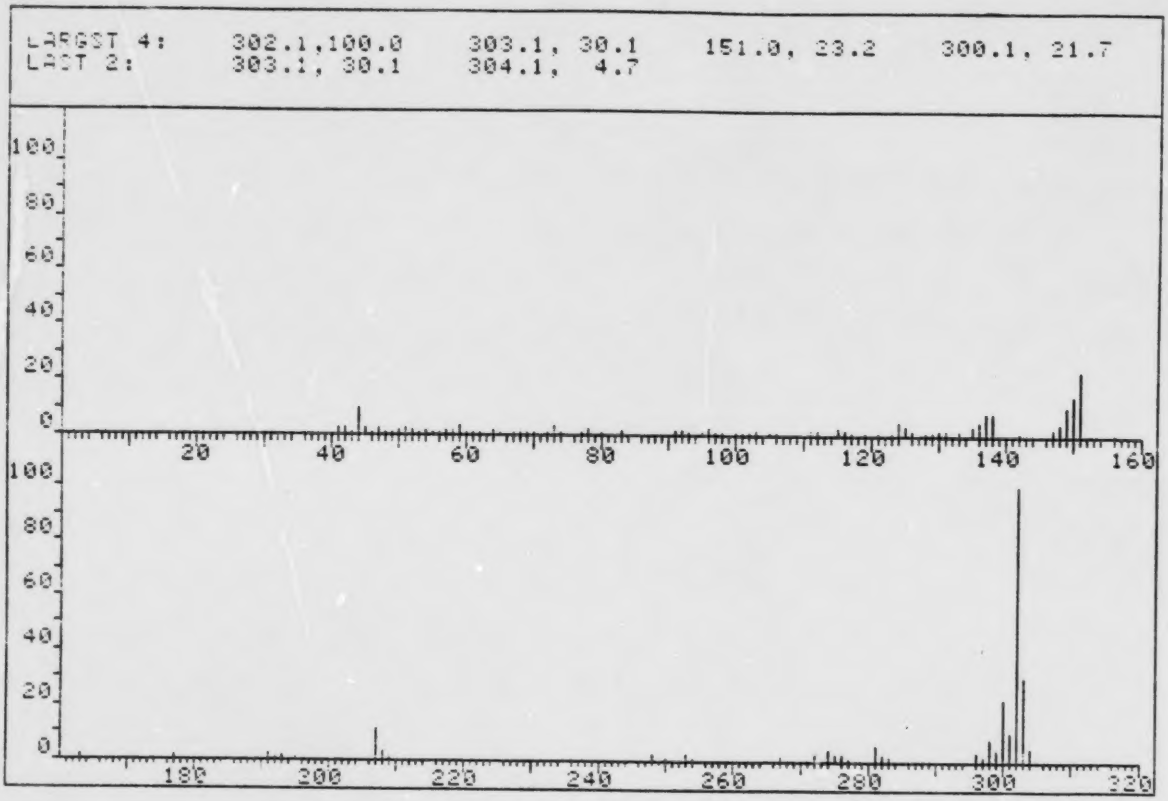


Figure B-13. Chromatogram by GC/MS for dibenzo(a,i)pyrene (t_R = 24.9 min).

Temperature program:

40 °C, 2 min isothermal
40 to 300 °C at 30 °C/min
300 °C, 10 min isothermal



```
LARGST 4:      302.1,100.0     303.1, 30.1     151.0, 23.2     300.1, 21.7
LAST 2:        303.1, 30.1     304.1,  4.7
```

Figure B-14. Mass spectrum for dibenzo(a,i)pyrene.

TABLE B-6. KEY IONS AND RELATIVE ABUNDANCES FOR DIBENZO(a,i)PYRENE

M/Z	Abun-dance	M/Z	Abun-dance	M/Z	Abun-dance
40.9	2.7	79.8	.7	141.7	.9
42.2	2.4	82.8	1.5	147.1	2.2
43.1	.9	91.2	1.3	147.9	4.6
44.0	10.0	92.1	1.9	149.0	10.6
45.0	1.2	93.1	.7	150.0	14.5
45.6	2.4	95.1	.7	151.0	23.2
46.4	.7	96.0	2.7	155.9	.7
47.1	2.1	97.2	.9	163.0	1.5
47.4	1.0	97.7	1.0	177.0	1.5
48.3	.7	98.2	.7	191.0	2.2
48.7	.9	99.7	.1	192.1	.7
49.1	.9	100.5	.9	193.0	1.5
49.6	.9	101.3	.9	195.0	.7
50.1	1.6	101.9	.7	207.0	10.8
50.8	.7	103.0	1.9	208.1	2.8
51.3	2.2	105.2	.7	208.9	1.6
52.3	1.8	105.6	.7	248.0	1.8
53.6	1.0	106.0	.9	250.0	.9
54.1	1.6	111.2	1.6	253.0	1.9
55.1	1.0	111.5	.7	254.0	.9
56.2	1.0	112.1	1.6	267.0	1.5
57.2	1.5	115.0	2.2	272.1	1.9
57.9	.9	115.9	1.5	274.1	3.5
58.3	1.5	117.1	.7	275.1	1.8
58.8	2.8	118.7	1.0	276.2	1.8
60.6	.9	119.3	.7	277.1	.7
61.6	.7	121.0	.6	281.1	5.0
62.1	.9	123.4	.9	282.0	1.9
64.0	1.5	124.1	4.9	283.1	1.6
65.2	.1	124.9	3.7	296.1	3.1
67.0	1.0	125.7	1.6	297.0	1.6
67.7	.9	127.9	.7	298.1	7.5
69.0	.7	128.7	.7	299.1	4.0
69.8	.7	129.9	1.5	300.1	21.7
72.0	.7	130.8	1.5	301.2	9.9
73.1	3.2	133.2	1.9	302.1	100.0
74.0	1.0	135.0	3.7	303.1	30.1
74.5	1.2	136.3	4.7	304.1	4.7
77.1	1.0	137.1	7.8	331.0	.7
78.1	2.4	138.1	8.1	354.2	.7

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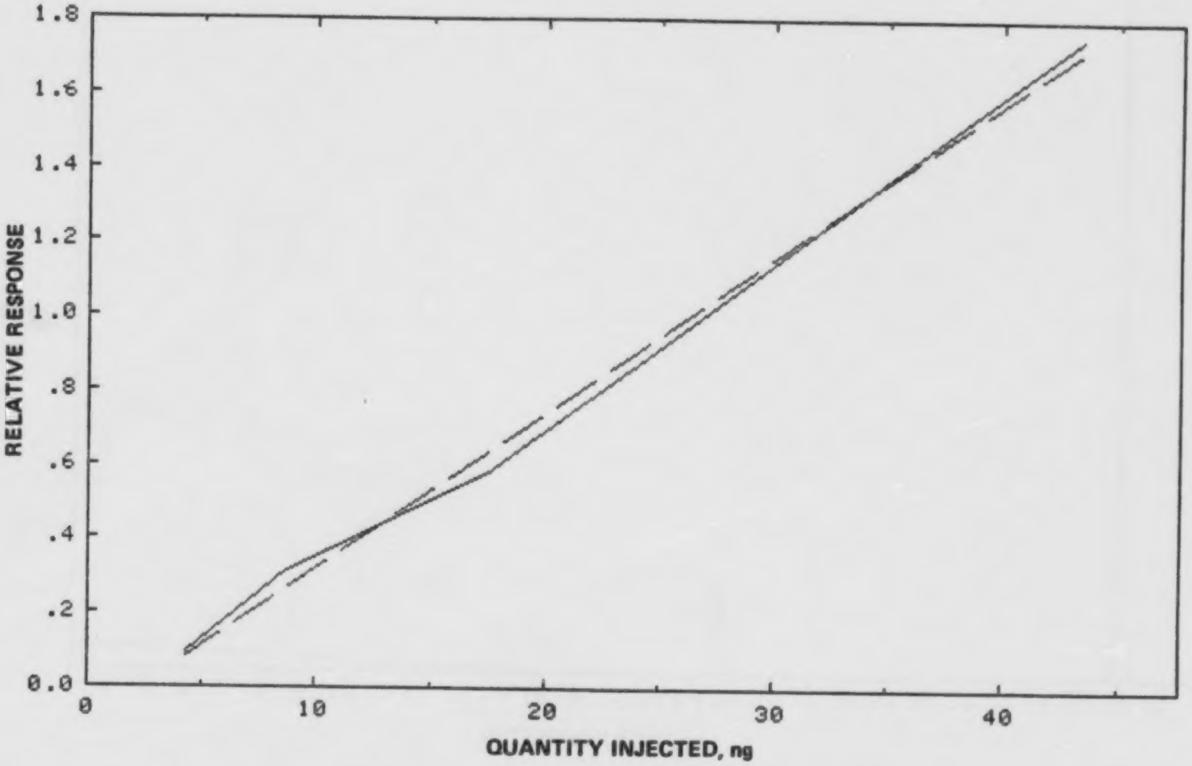

Figure B-15. Calibration curve for the determination of dibenzo(a,i)pyrene by GC/MS.

Range: 4-40 ng
Correlation coefficient: 0.998
Slope: 4.19×10^{-2}
y-Intercept: -9.87×10^{-2}

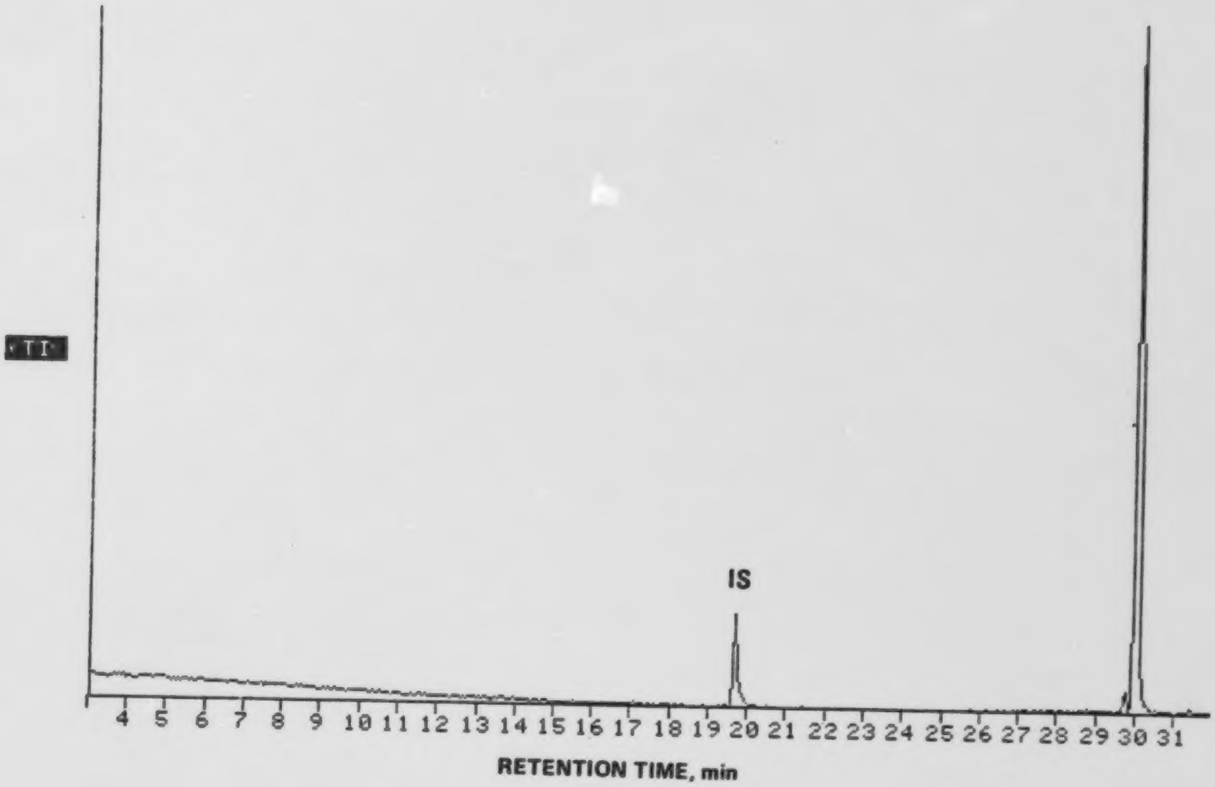

Figure B-16. Chromatogram by GC/MS for hexachlorophene (t_R = 30.0 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 10 min isothermal

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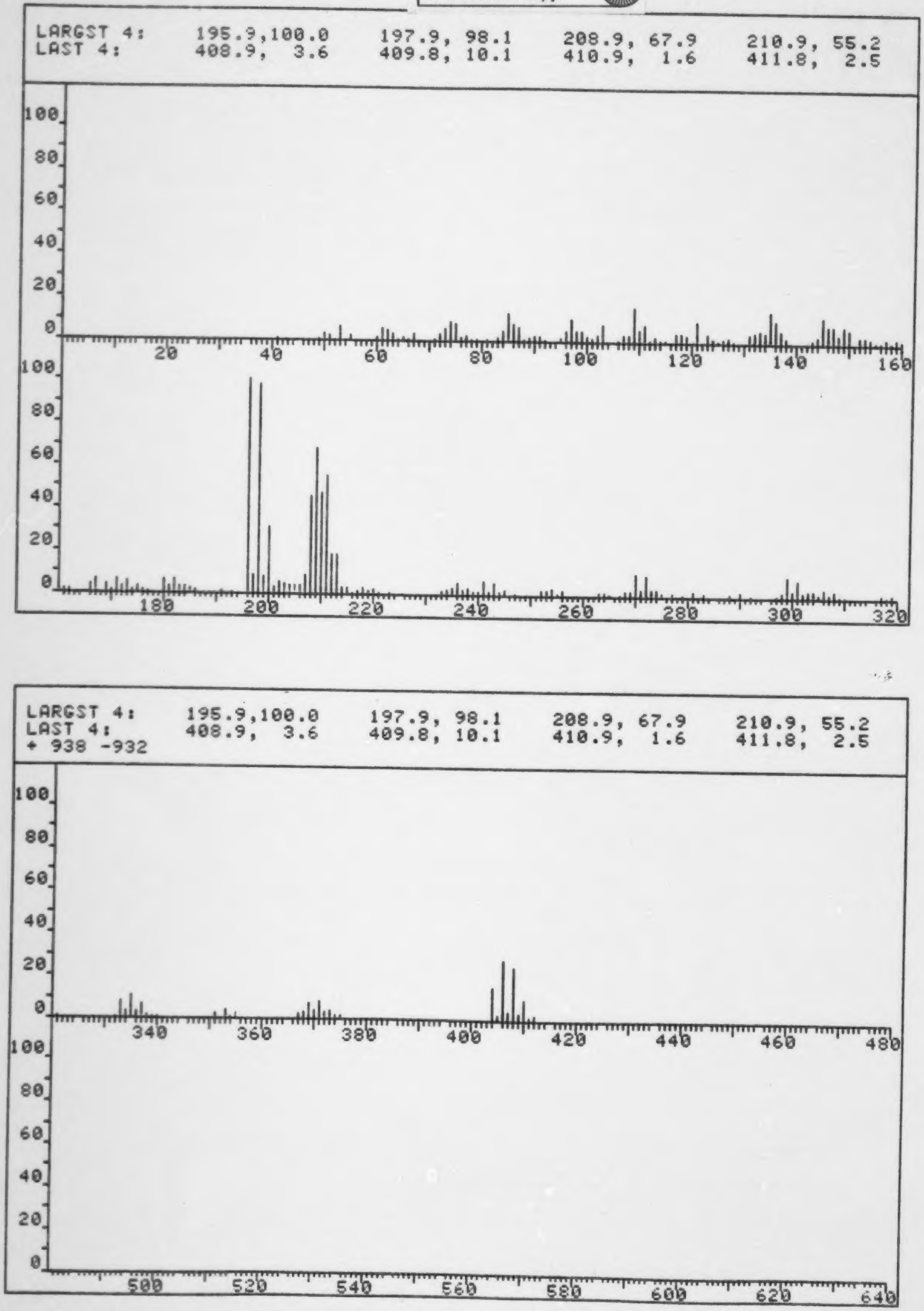


```
LARGST 4:    195.9,100.0    197.9, 98.1    208.9, 67.9    210.9, 55.2
LAST 4:      408.9,   3.6   409.8, 10.1    410.9,  1.6    411.8,  2.5
```

```
LARGST 4:    195.9,100.0    197.9, 98.1    208.9, 67.9    210.9, 55.2
LAST 4:      408.9,   3.6   409.8, 10.1    410.9,  1.6    411.8,  2.5
+ 938 -932
```

Figure B-17. Mass spectrum for hexachlorophene.

TABLE B-7. KEY IONS AND RELATIVE ABUNDANCES FOR HEXACHLOROPHENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
50.0	5.6	110.0	7.4	167.5	10.6	241.0	5.9
53.1	9.1	111.0	10.0	169.0	5.0	243.0	5.0
61.0	7.2	117.1	6.5	171.0	7.8	269.9	10.0
62.1	8.1	118.1	6.9	173.0	7.0	270.9	5.7
63.0	7.2	119.0	5.0	180.0	6.1	271.9	9.6
72.0	6.5	120.6	12.0	182.0	6.9	298.9	7.6
73.0	9.8	122.9	5.2	195.9	100.0	301.0	6.5
74.0	14.6	132.0	5.4	197.0	9.3	333.0	12.2
75.1	11.7	134.0	7.6	197.9	95.6	334.9	16.7
84.0	6.3	135.0	17.2	198.9	8.0	336.9	9.6
85.1	19.8	135.9	13.1	199.9	32.2	366.9	6.1
86.0	12.6	137.1	9.1	201.9	6.5	367.9	6.3
87.0	10.6	144.9	13.0	205.0	5.4	368.9	9.8
96.0	8.0	146.0	8.9	207.0	9.6	369.9	10.6
97.0	14.4	147.0	8.5	207.9	48.5	370.9	9.1
98.0	7.6	148.0	5.6	208.9	58.7	371.9	5.9
99.0	6.7	149.4	7.8	209.9	44.6	403.9	10.0
102.0	5.0	150.5	7.0	210.9	53.0	405.9	15.2
103.1	12.6	152.0	5.4	211.9	16.9	407.8	13.5
107.0	5.0	152.9	5.7	212.9	15.6	409.8	5.9
109.0	23.1	166.5	7.2	236.0	5.4		

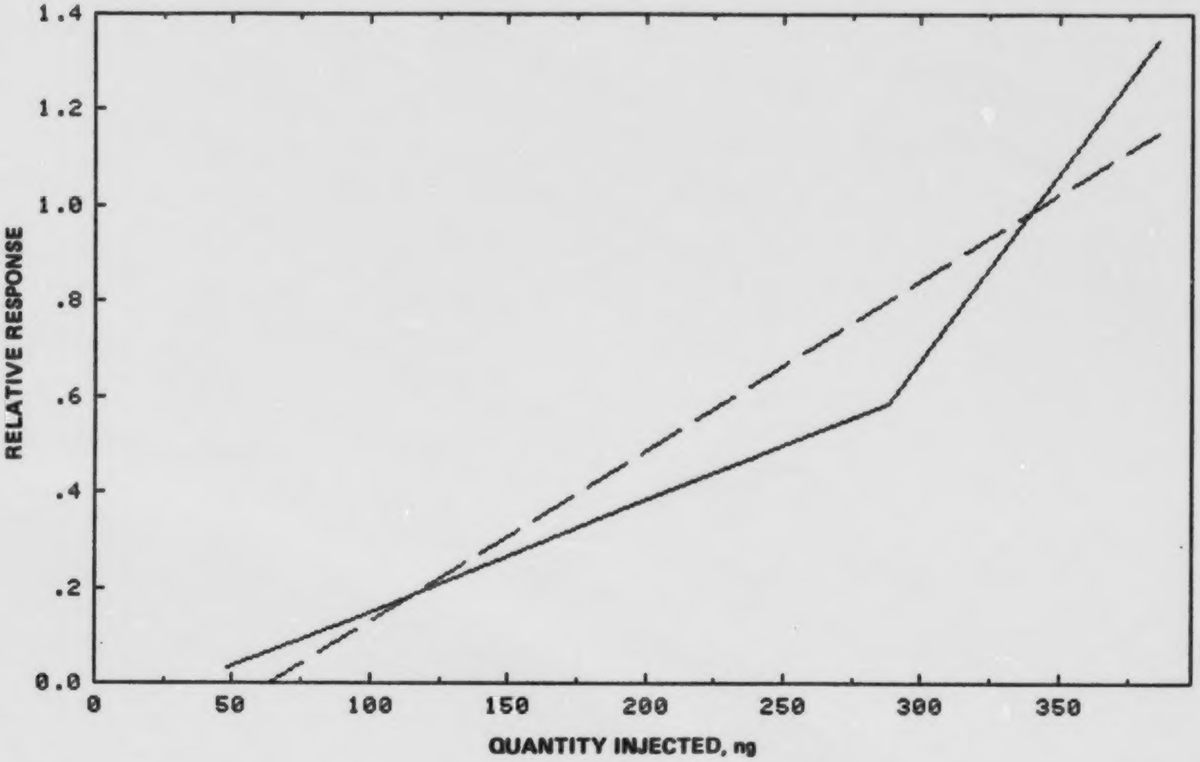


Figure B-18. Calibration curve for the determination of hexachlorophene by GC/MS.

Range: 80-400 ng
Correlation coefficient: 0.952
Slope: 3.59×10^{-3}
y-Intercept: -2.33×10^{-1}

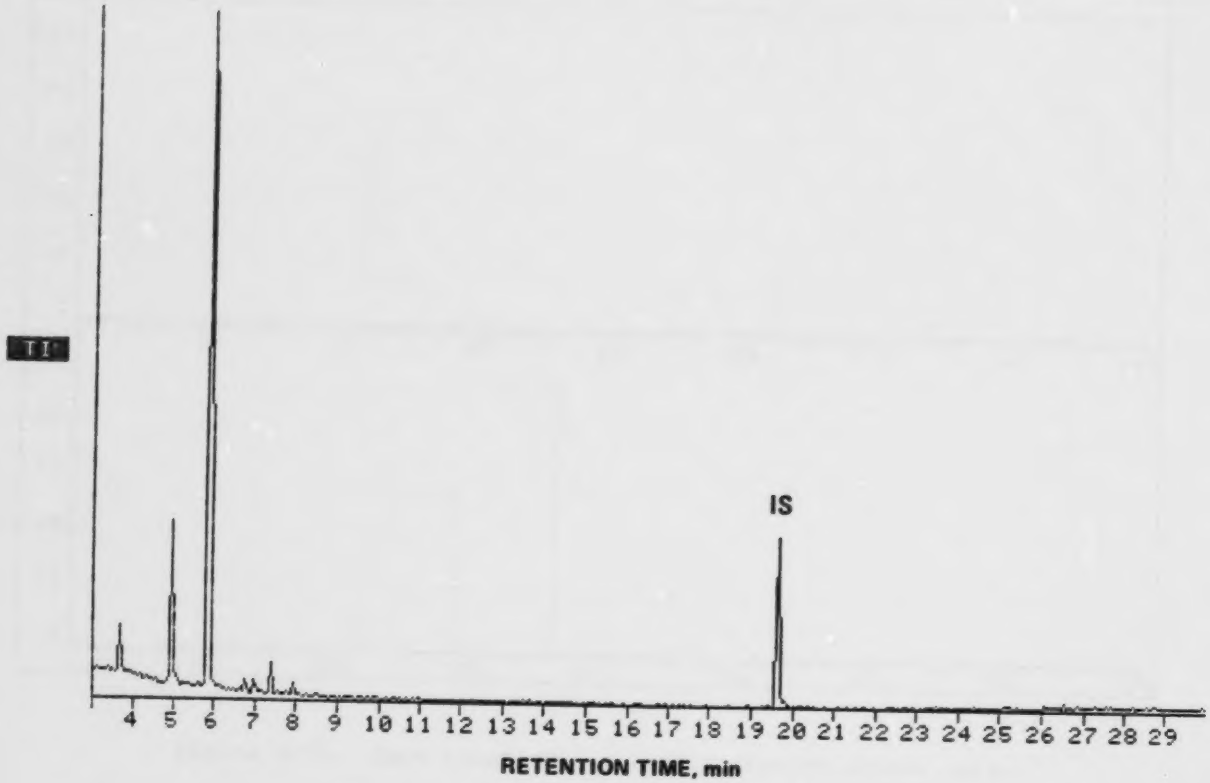
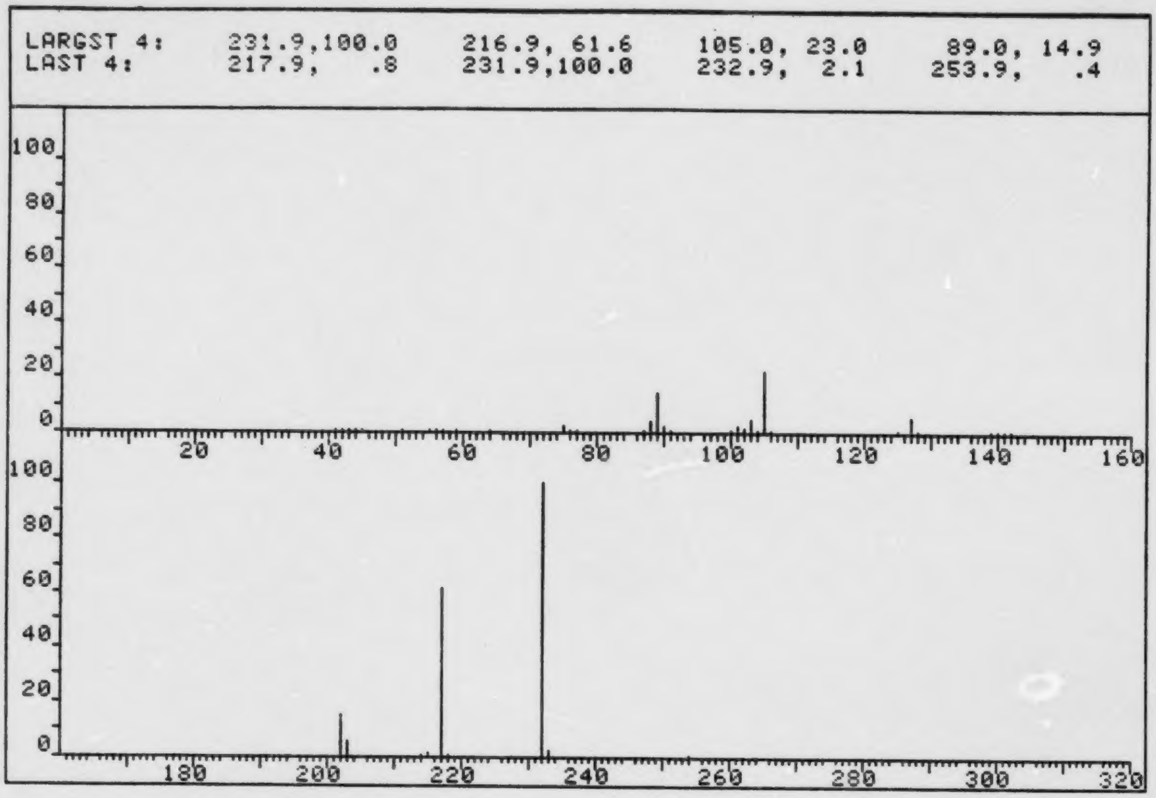


Figure B-19. Chromatogram by GC/MS for hydroxydimethylarsine oxide (t_R = 5.9 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 10 min isothermal



```
LARGST 4:     231.9,100.0     216.9, 61.6     105.0, 23.0      89.0, 14.9
LAST 4:       217.9,    .8    231.9,100.0     232.9,  2.1     253.9,    .4
```

Figure B-20. Mass spectrum for hydroxydimethylarsine oxide.

TABLE B-8. KEY IONS AND RELATIVE ABUNDANCES FOR HYDROXYDIMETHYLARSINE OXIDE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.1	.6	86.9	.6	127.9	.8
42.0	.3	87.9	4.3	139.0	.3
43.1	.7	89.0	14.9	140.0	.6
44.0	1.0	90.0	2.7	141.0	.2
45.1	.2	91.0	.2	142.0	.3
50.9	.2	99.9	.5	201.8	14.7
54.7	.2	101.0	2.3	202.9	5.3
56.1	.4	101.9	1.4	213.9	.7
57.1	.7	103.0	5.0	214.8	1.1
59.2	.2	104.0	.4	216.9	61.6
64.2	.3	105.0	23.0	217.9	.8
75.0	2.2	106.1	.5	231.9	100.0
75.9	.6	125.0	.7	232.9	2.1
77.0	.6	127.0	5.6	253.9	.4

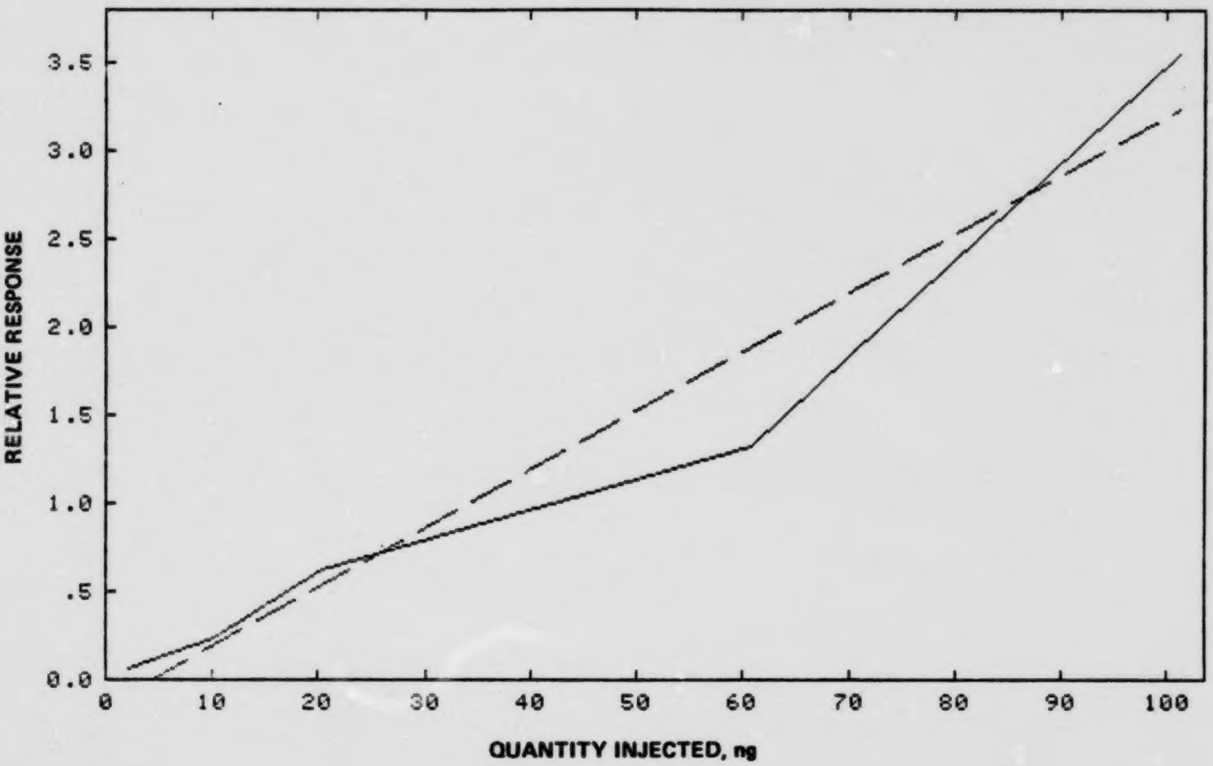


Figure B-21. Calibration curve for the determination of hydroxydimethylarsine oxide by GC/MS.

Range: 6-100 ng
Correlation coefficient: 0.973
Slope: 3.33×10^{-2}
y-Intercept: -1.36×10^{-1}

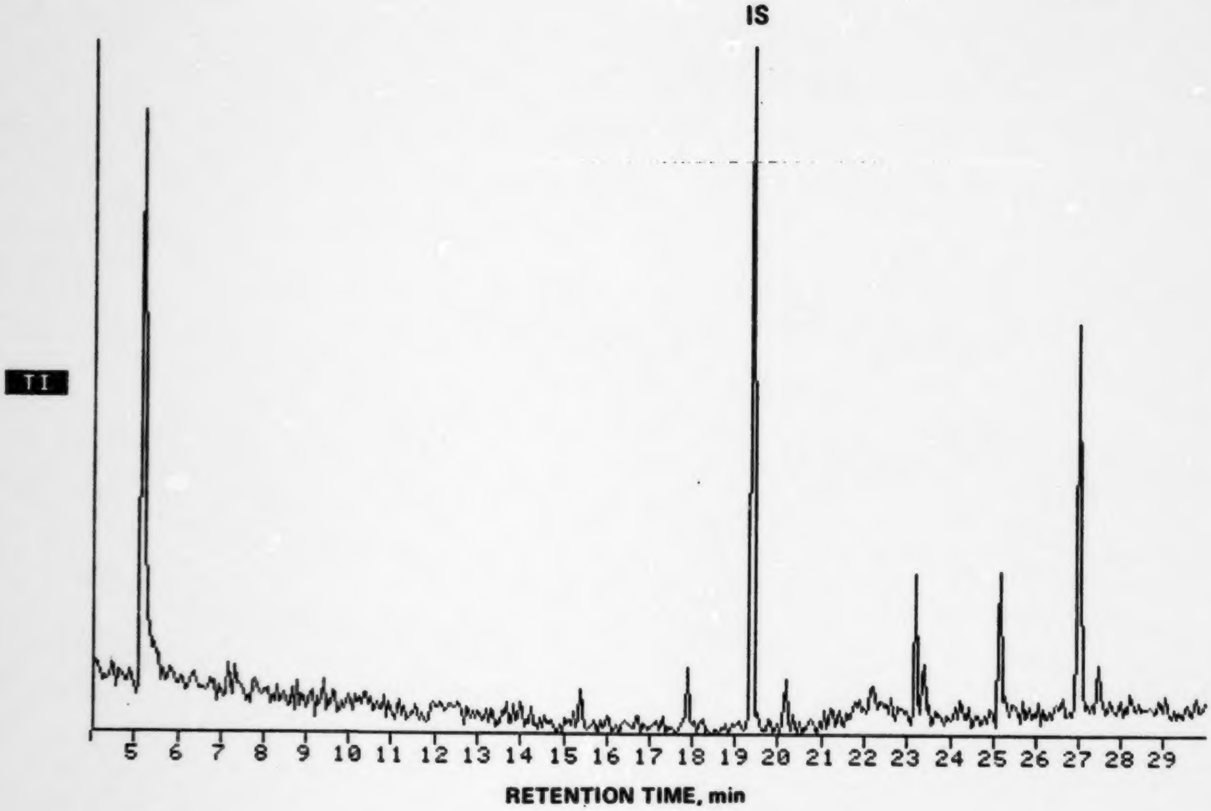
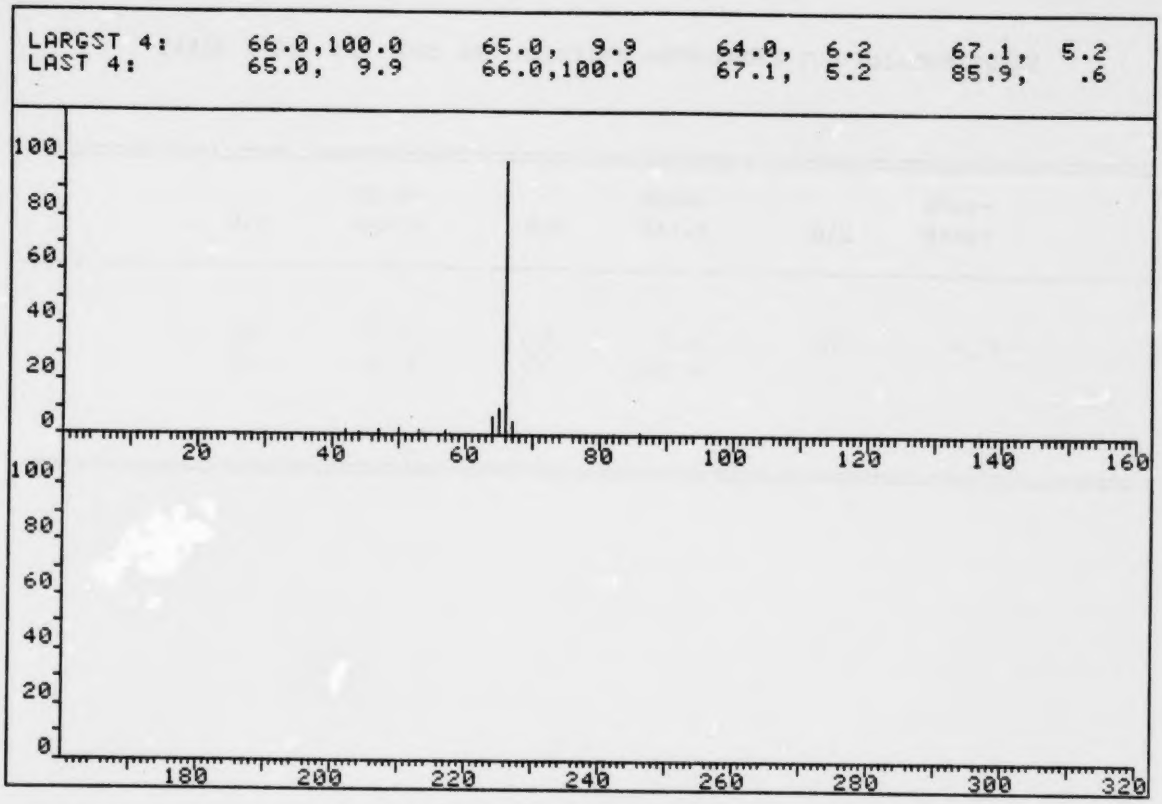


Figure B-22. Chromatogram by GC/MS for malononitrile (t_R = 5.2 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 10 min isothermal



```
LARGST 4:      66.0,100.0      65.0,  9.9      64.0,  6.2      67.1,  5.2
LAST 4:        65.0,  9.9      66.0,100.0      67.1,  5.2      85.9,   .6
```

Figure B-23. Mass spectrum for malononitrile.

TABLE B-9. KEY IONS AND RELATIVE ABUNDANCES FOR MALONONITRILE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
50	2.8	65	9.6	67	4.9
64	6.9	66	100.0		

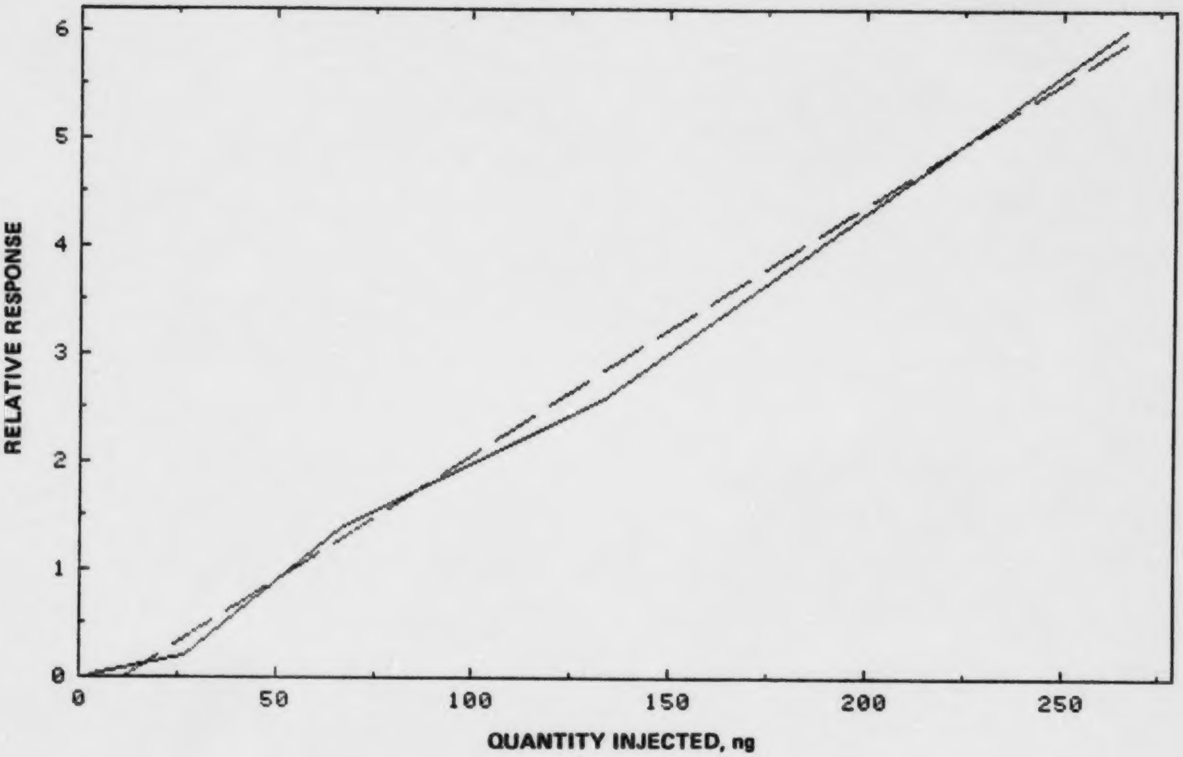


Figure B-24. Calibration curve for the determination of malononitrile by GC/MS.

Range: 20-250 ng
Correlation coefficient: 0.997
Slope: 2.31×10^{-2}
y-Intercept: -2.45×10^{-1}

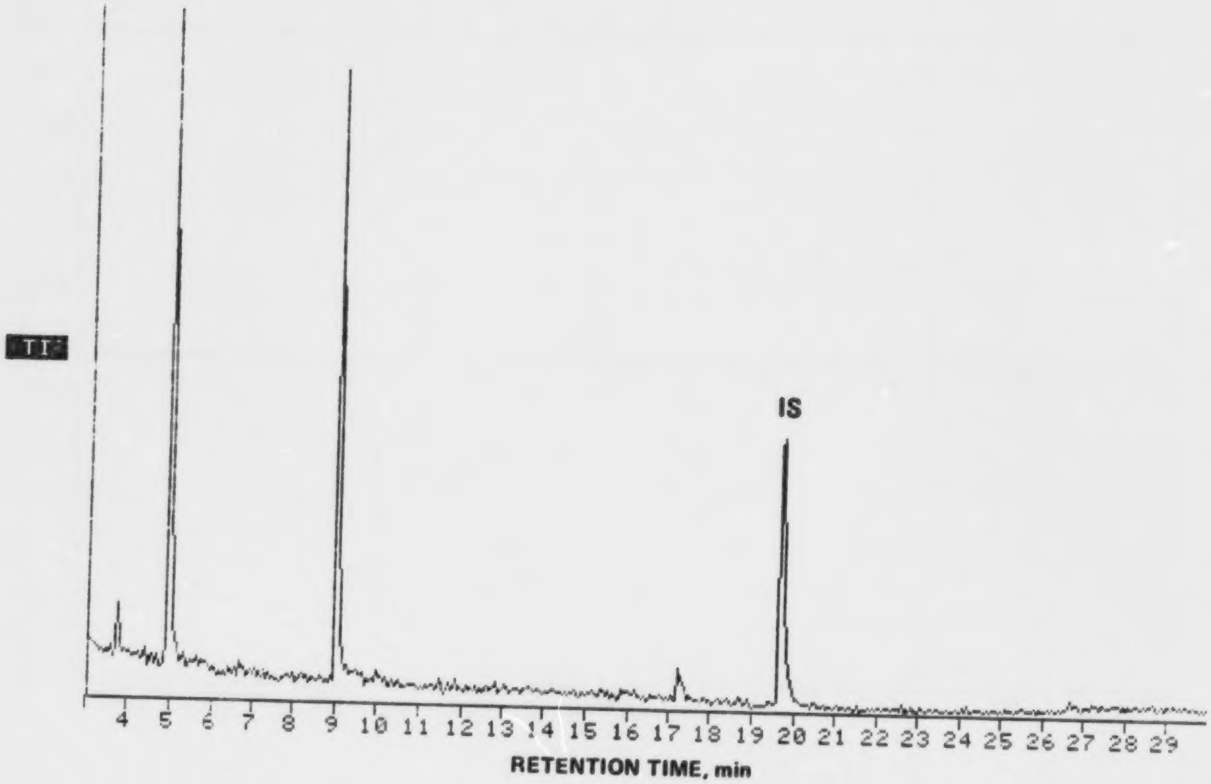


Figure B-25. Chromatogram by GC/MS for phenylmercury acetate (t_R = 9.1 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 10 min isothermal

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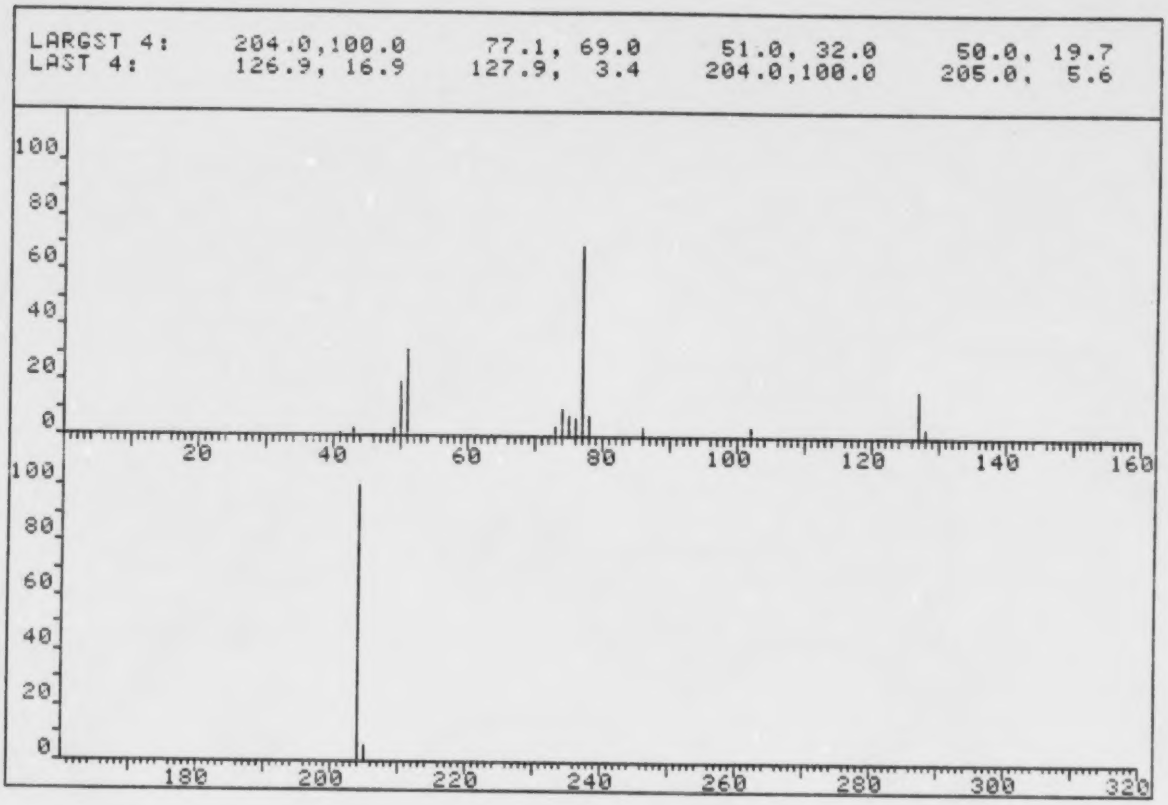


```
LARGST 4:     204.0,100.0      77.1, 69.0      51.0, 32.0       50.0, 19.7
LAST 4:       126.9, 16.9     127.9,  3.4     204.0,100.0      205.0,  5.6
```

Figure B-26. Mass spectrum for phenylmercury acetate.

TABLE B-10. KEY IONS AND RELATIVE ABUNDANCES FOR PHENYLMERCURY ACETATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.0	6.0	57.1	6.0	86.1	3.1
43.0	5.6	73.0	3.4	102.0	3.8
44.0	7.5	74.1	10.0	126.9	16.9
49.0	5.6	75.1	7.2	127.9	3.4
50.0	23.8	76.1	6.6	204.0	100.0
51.0	32.0	77.1	73.4	205.0	5.6
56.0	4.1	78.1	6.9		

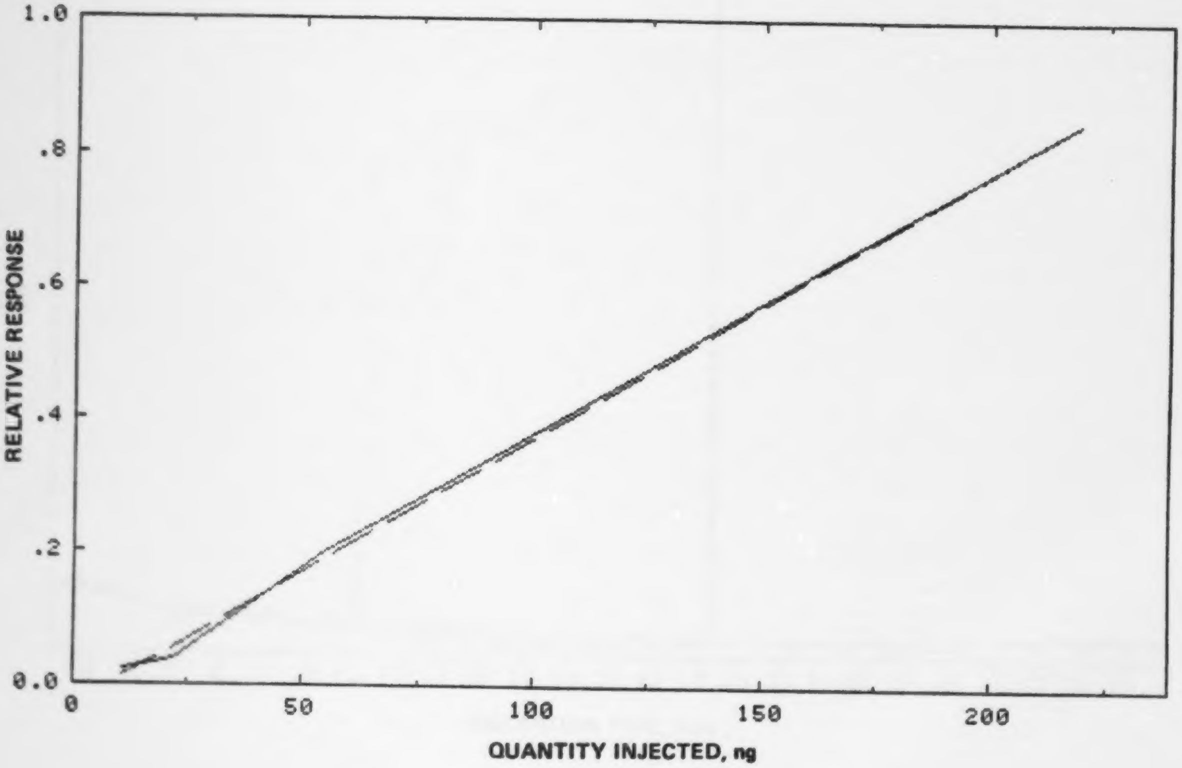


Figure B-27. Calibration curve for the determination of phenylmercury acetate by GC/MS.

Range: 10-200 ng
Correlation coefficient: 0.999
Slope: 4.02×10^{-3}
y-Intercept: -3.06×10^{-2}

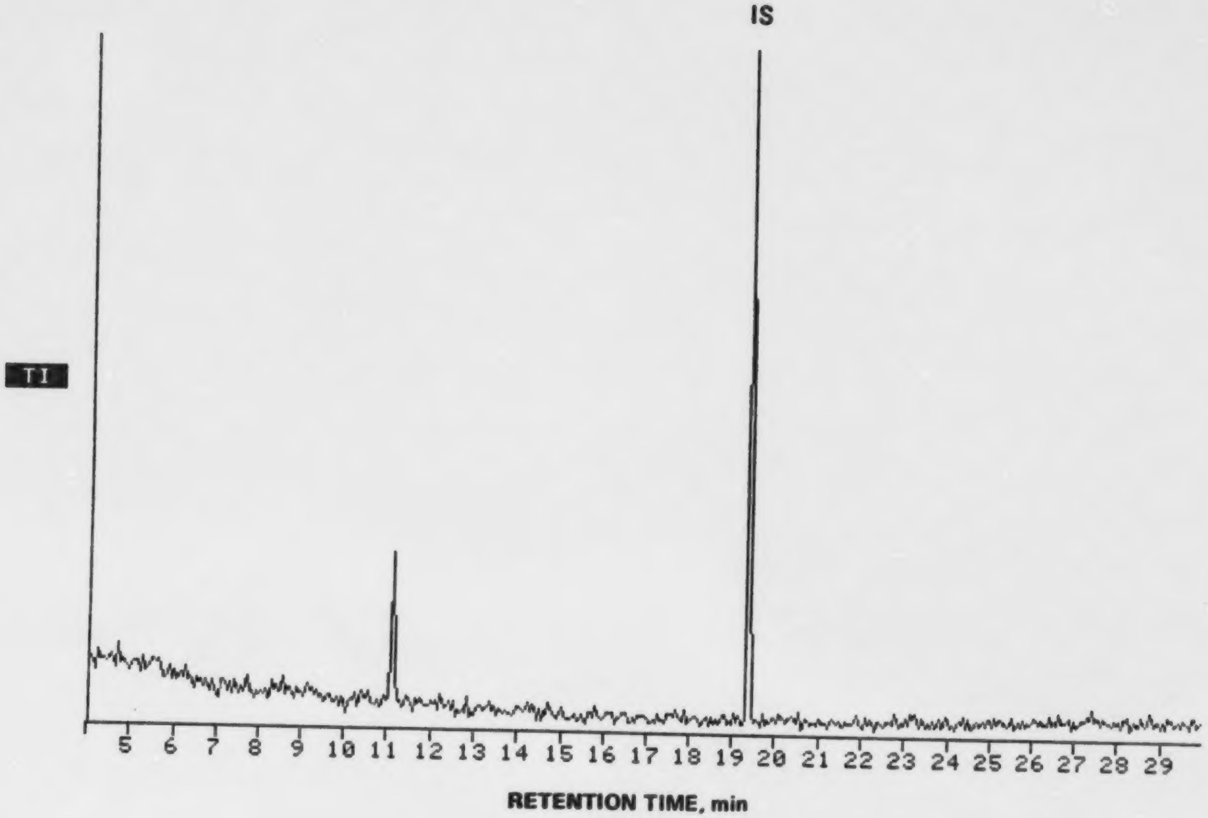
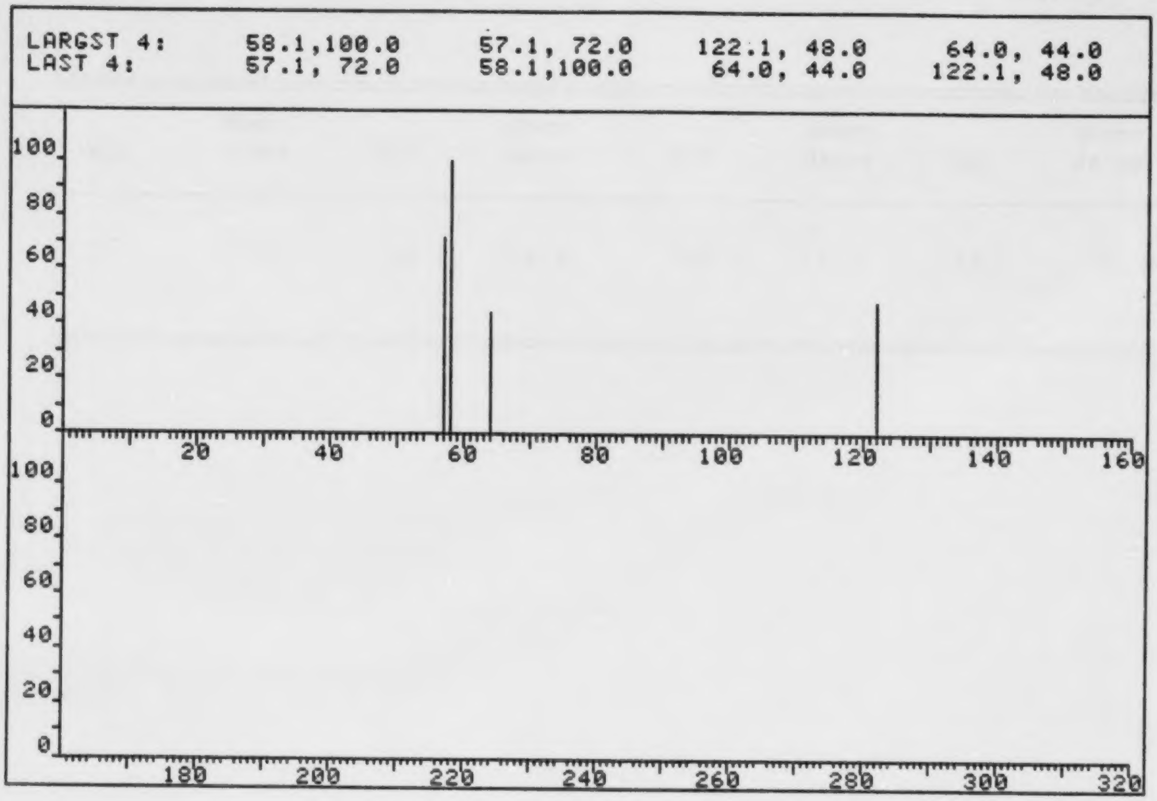


Figure B-28. Chromatogram by GC/MS for 1,3-propane sultone (t_R = 11.1 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 10 min isothermal



```
LARGST 4:     58.1,100.0      57.1, 72.0     122.1, 48.0       64.0, 44.0
LAST 4:       57.1, 72.0      58.1,100.0      64.0, 44.0      122.1, 48.0
```

Figure B-29. Mass spectrum for 1,3-propane sultone.

TABLE B-11. KEY IONS AND RELATIVE ABUNDANCES FOR 1,3-PROPANE SULTONE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
57	72.0	58	100.0	64	44.0	122	48.0

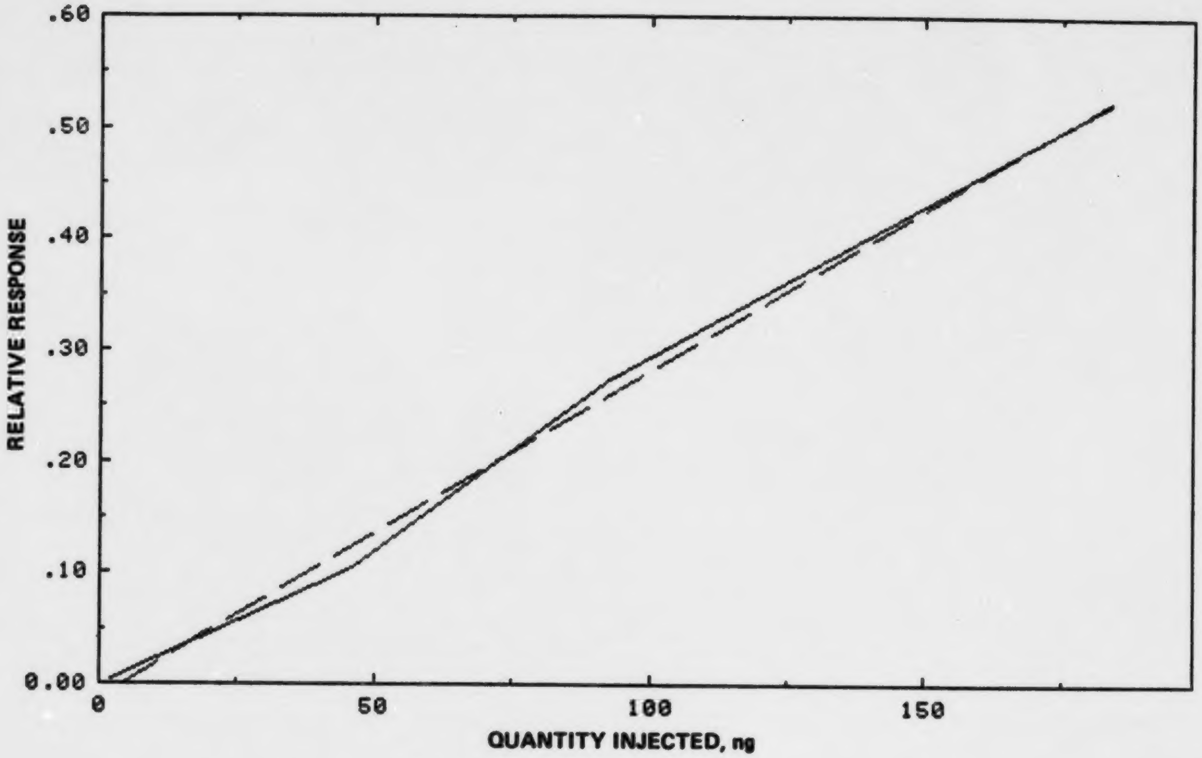


Figure B-30. Calibration curve for the determination of 1,3-propane sultone by GC/MS.

Range: 5-180 ng
Correlation coefficient: 0.998
Slope: 2.92×10^{-3}
y-Intercept: -1.03×10^{-2}

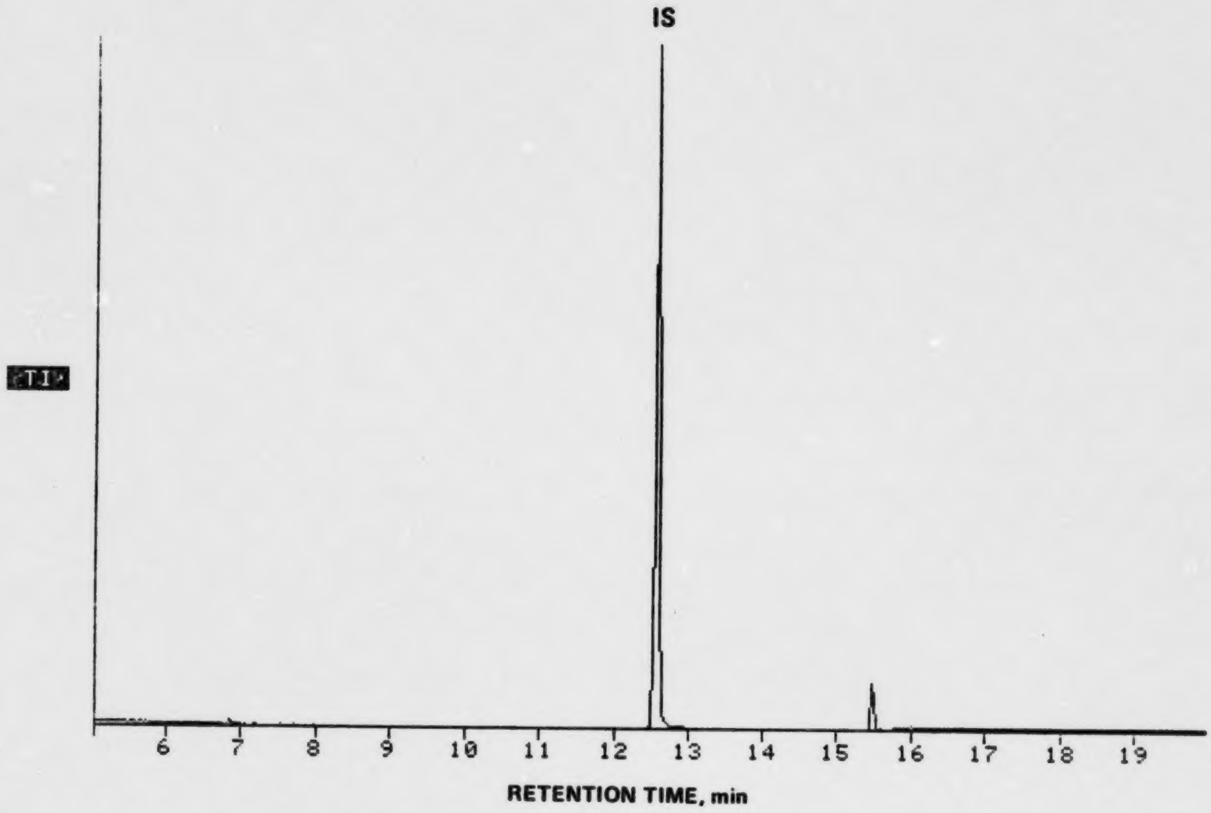


Figure B-31. Chromatogram by GC/MS for 2,3,7,8-tetrachlorodibenzo-p-dioxin (t_R = 15.5 min).

Temperature program:

60 °C, 4 min isothermal
60 to 300 °C at 20 °C/min
300 °C, 10 min isothermal

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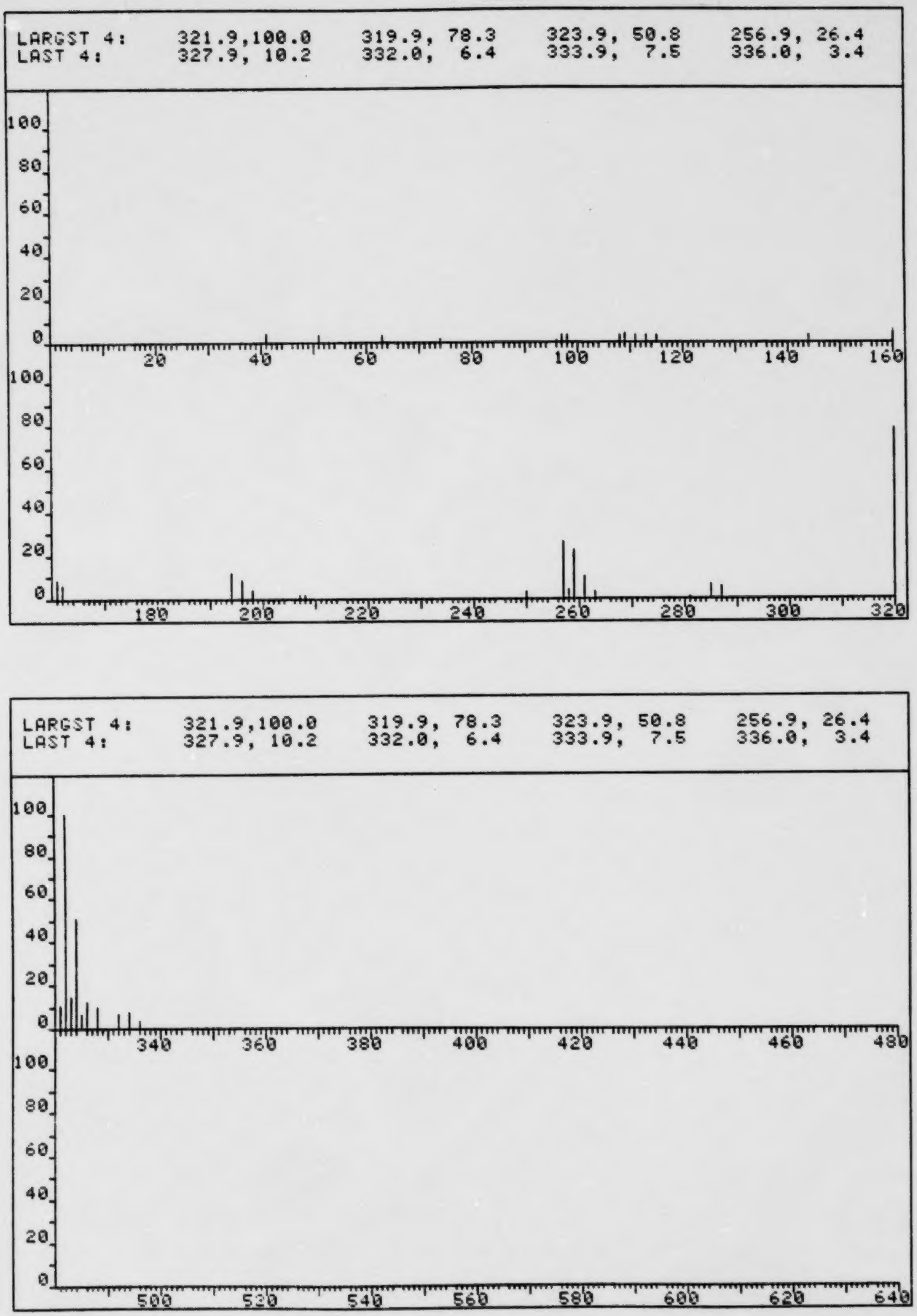


```
LARGST 4:     321.9,100.0     319.9, 78.3     323.9, 50.8     256.9, 26.4
LAST 4:       327.9, 10.2     332.0,  6.4     333.9,  7.5     336.0,  3.4
```

```
LARGST 4:     321.9,100.0     319.9, 78.3     323.9, 50.8     256.9, 26.4
LAST 4:       327.9, 10.2     332.0,  6.4     333.9,  7.5     336.0,  3.4
```

Figure B-32. Mass spectrum for 2,3,7,8-tetrachlorodibenzo-p-dioxin.

TABLE B-12. KEY IONS AND RELATIVE ABUNDANCES FOR 2,3,7,8-TETRACHLORODIBENZO-*p*-DIOXIN

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
40.0	11.8	115.1	3.5	263.0	3.2
41.0	3.8	143.9	3.2	281.0	4.2
44.0	13.1	159.9	5.8	285.0	6.1
50.1	3.5	161.0	8.0	287.0	5.1
51.0	3.5	161.9	5.4	319.9	78.3
57.1	3.5	193.9	10.9	320.9	9.9
63.1	3.2	195.9	8.3	321.9	100.0
72.8	3.8	198.0	3.5	322.9	14.1
74.0	7.3	207.1	12.1	323.9	47.9
96.0	3.5	208.0	4.2	324.9	6.1
97.0	7.0	250.0	3.2	325.9	11.5
98.0	3.2	256.9	24.9	327.9	9.6
107.9	3.2	258.1	3.8	332.0	6.1
109.1	3.8	258.9	21.4	333.9	7.0
110.9	3.2	261.0	9.3	336.0	3.2
113.0	3.2				

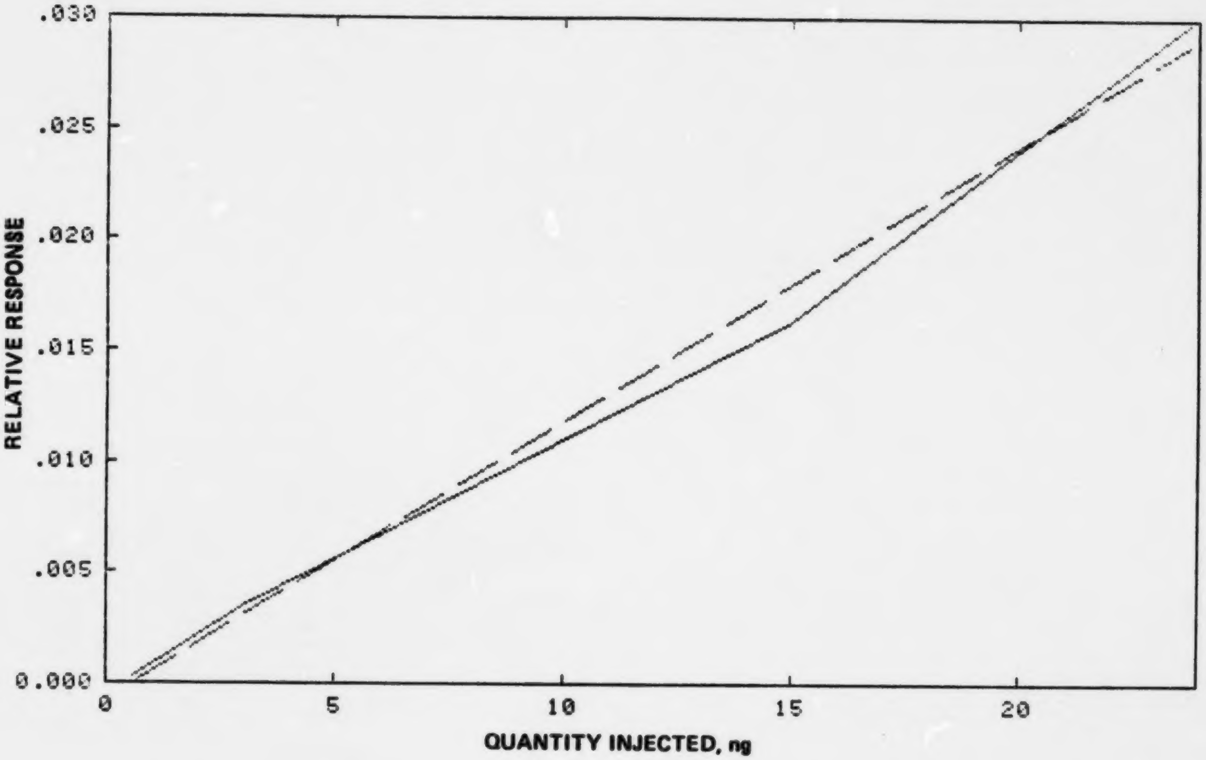


Figure B-33. Calibration curve for the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin by GC/MS.

Range: 1-25 ng
Correlation coefficient: 0.999
Slope: 7.91×10^{-3}
y-Intercept: -8.47×10^{-3}

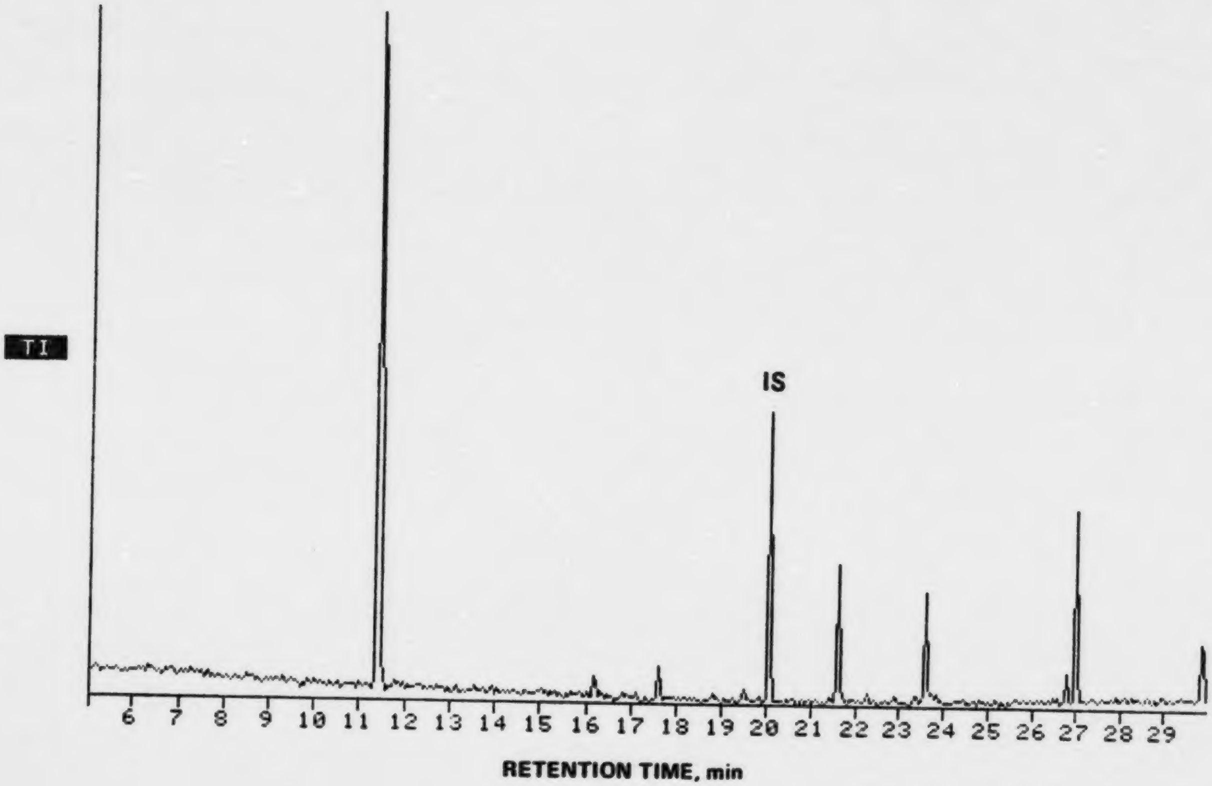
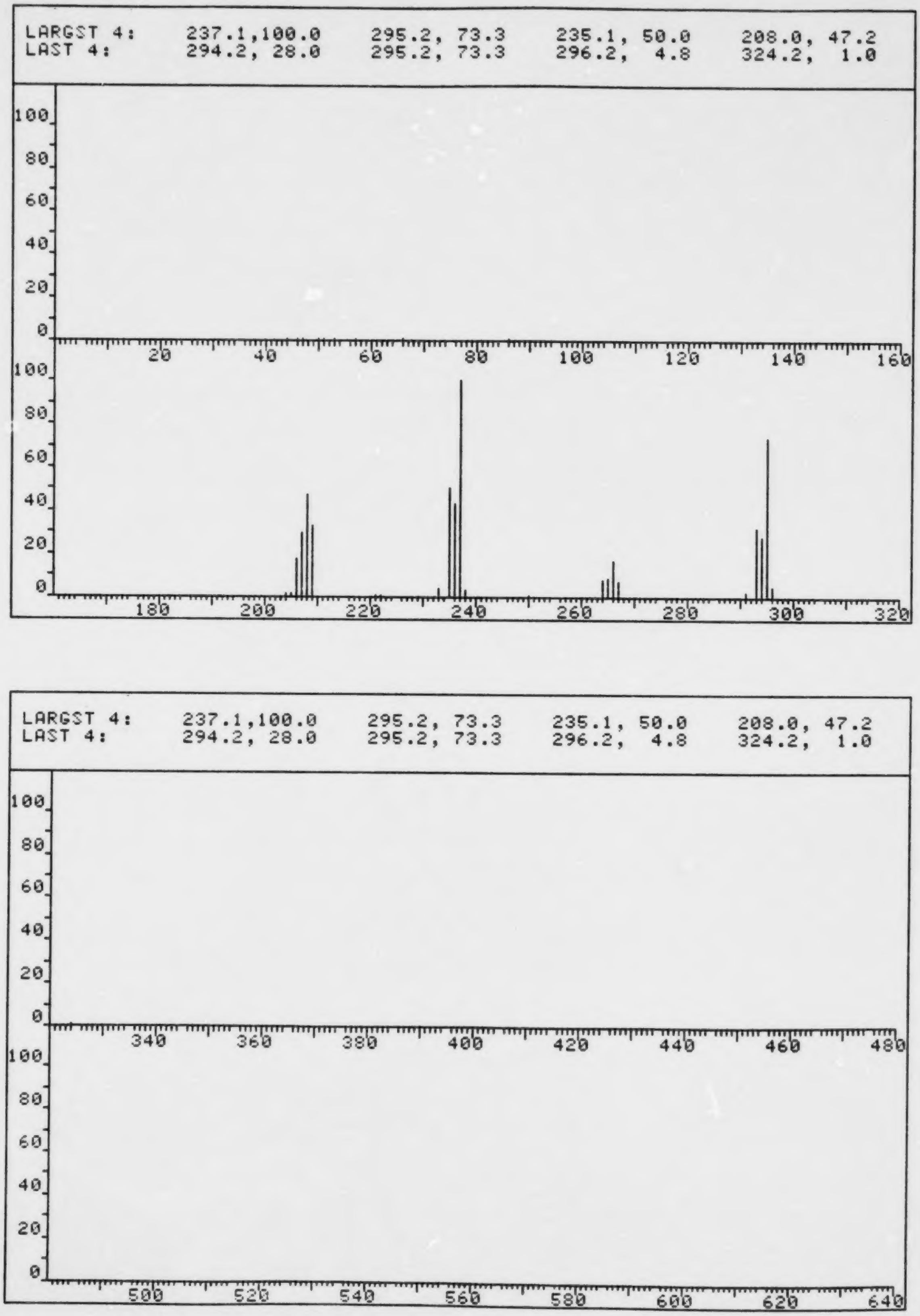


Figure B-34. Chromatogram by GC/MS for tetraethyl lead (t_R = 11.4 min).

Temperature program:

40 °C, 3 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 10 min isothermal



```
LARGST 4:     237.1,100.0     295.2, 73.3     235.1, 50.0     208.0, 47.2
LAST 4:       294.2, 28.0     295.2, 73.3     296.2,  4.8     324.2,  1.0
```

```
LARGST 4:     237.1,100.0     295.2, 73.3     235.1, 50.0     208.0, 47.2
LAST 4:       294.2, 28.0     295.2, 73.3     296.2,  4.8     324.2,  1.0
```

Figure B-35. Mass spectrum for tetraethyl lead.

TABLE B-13. KEY IONS AND RELATIVE ABUNDANCES FOR TETRAETHYL LEAD

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
206	20.2	233	3.7	264	5.5	293	16.7
207	40.2	235	48.2	265	6.7	294	16.4
208	62.1	236	43.0	266	12.9	295	40.9
209	40.5	237	100.0	267	5.1		

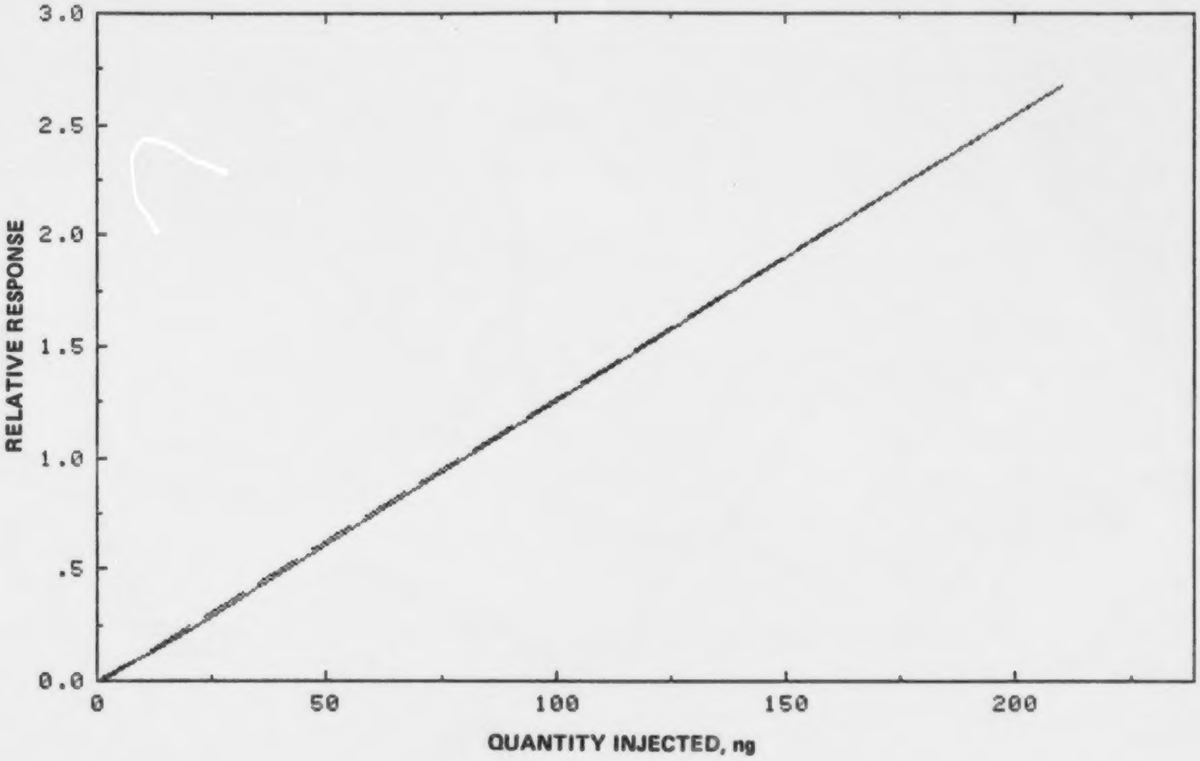


Figure B-36. Calibration curve for the determination of tetraethyl lead by GC/MS.

Range: 2-200 ng
Correlation coefficient: 0.999
Slope: 1.28×10^{-2}
y-Intercept: -1.39×10^{-2}

APPENDIX C

CHROMATOGRAMS, UV SPECTRA, AND CALIBRATION CURVES FOR HPLC/UV DETERMINATIONS

Index

Compound	Reference chromatogram Figure No.	Reference UV Figure No.	Reference calibration curve Figure No.
2-Acetylaminofluorene	C-1	C-2	C-3
Aflatoxin B-1	C-4	C-5	C-6
Aflatoxin B-2	C-7	C-8	C-9
Aflatoxin G-1	C-10	C-11	C-12
Aflatoxin G-2	C-13	C-14	C-15
Benzenearsonic acid	C-16	C-17	C-18
Benz(a)anthracene	C-19	C-20	C-21
Benzo(b)fluoranthene	C-22	C-23	C-24
Benzo(a)pyrene	C-25	C-26	C-27
Bis(2-ethylhexyl) phthalate	C-28	C-37	C-38
Butyl benzyl phthalate	C-28	C-33	C-34
Chrysene	C-41	C-42	C-43
Dibenz(a,j)acridine	C-44	C-45	C-46
Dibenz(a,h)anthracene	C-47	C-48	C-49
Dibenzo(a,i)pyrene	C-50	C-51	C-52
Diethyl phthalate	C-28	C-31	C-32
7,12-Dimethylbenz(a)anthracene	C-53	C-54	C-55
Dimethyl phthalate	C-28	C-29	C-30
Di-*n*-butyl phthalate	C-28	C-35	C-36
Di-*n*-octyl phthalate	C-28	C-39	C-40
Fluoranthene	C-56	C-57	C-58
Indeno(1,2,3-c,d)pyrene	C-59	C-60	C-61
3-Methylcholanthrene	C-62	C-63	C-64
Napthalene	C-65	C-66	C-67
Selenourea	C-68	C-69	C-70

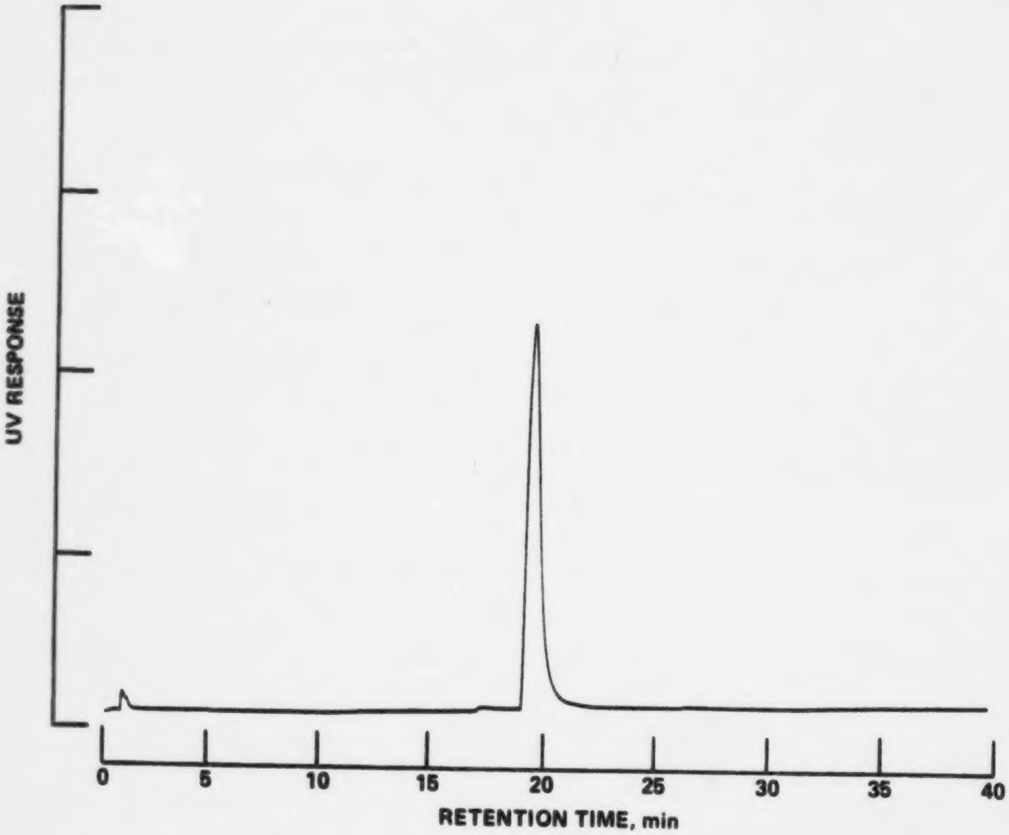


Figure C-1. Chromatogram by HPLC/UV for 2-acetylaminofluorene.

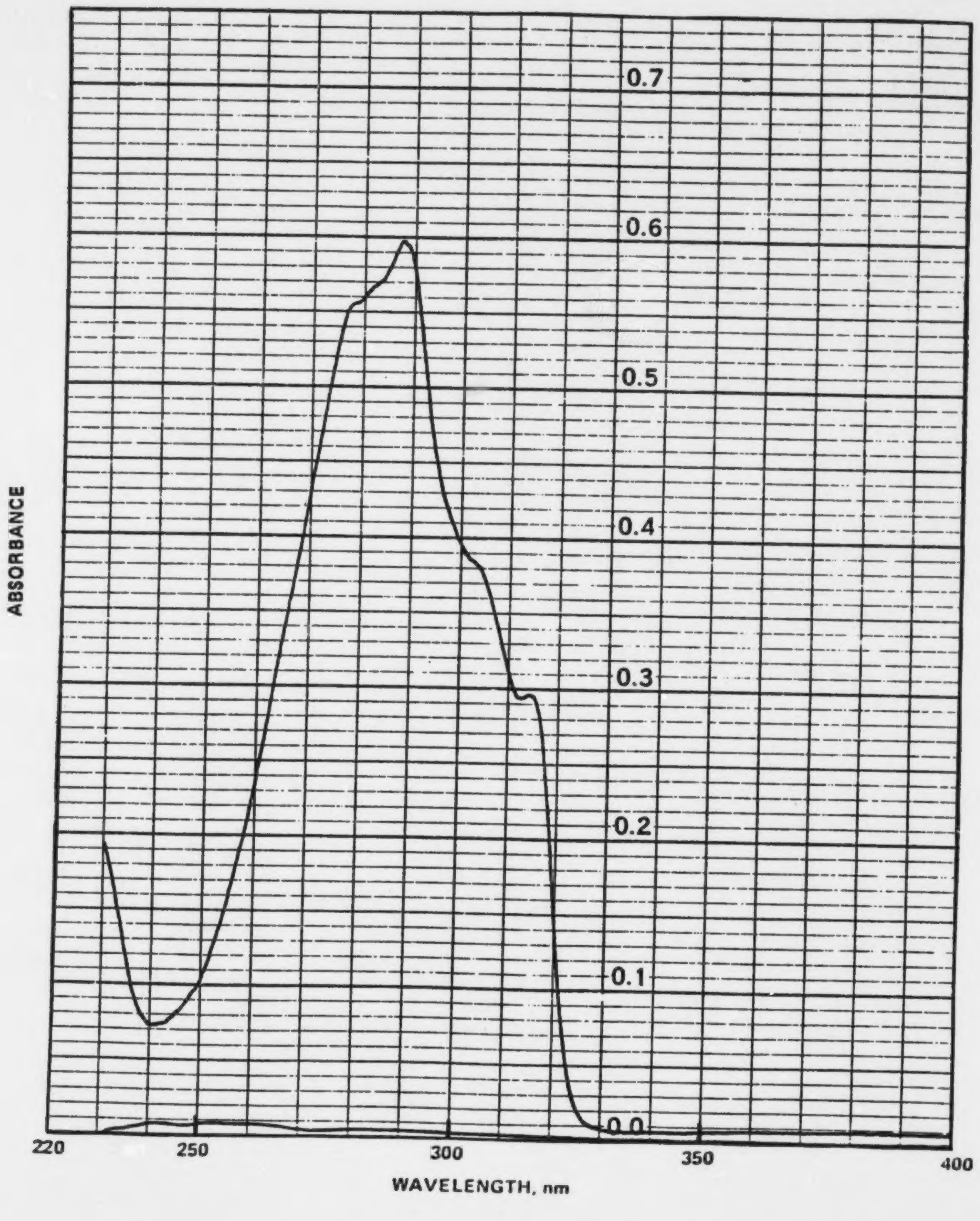


Figure C-2. UV spectrum of 2-acetylaminofluorene.

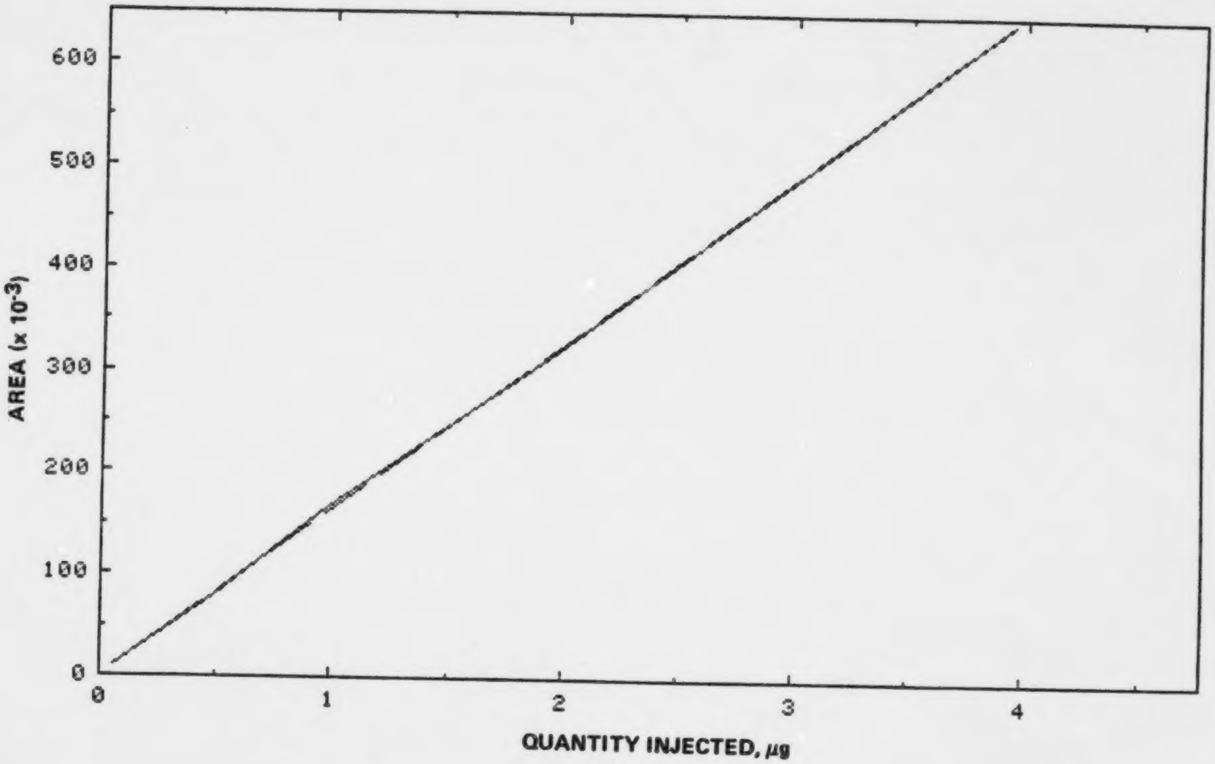


Figure C-3. Calibration curve for the determination of 2-acetylaminofluorene by HPLC/UV.

Range: 0.06-4 µg
Correlation coefficient: 0.999
Slope: 1.63×10^2
y-Intercept: 1.04

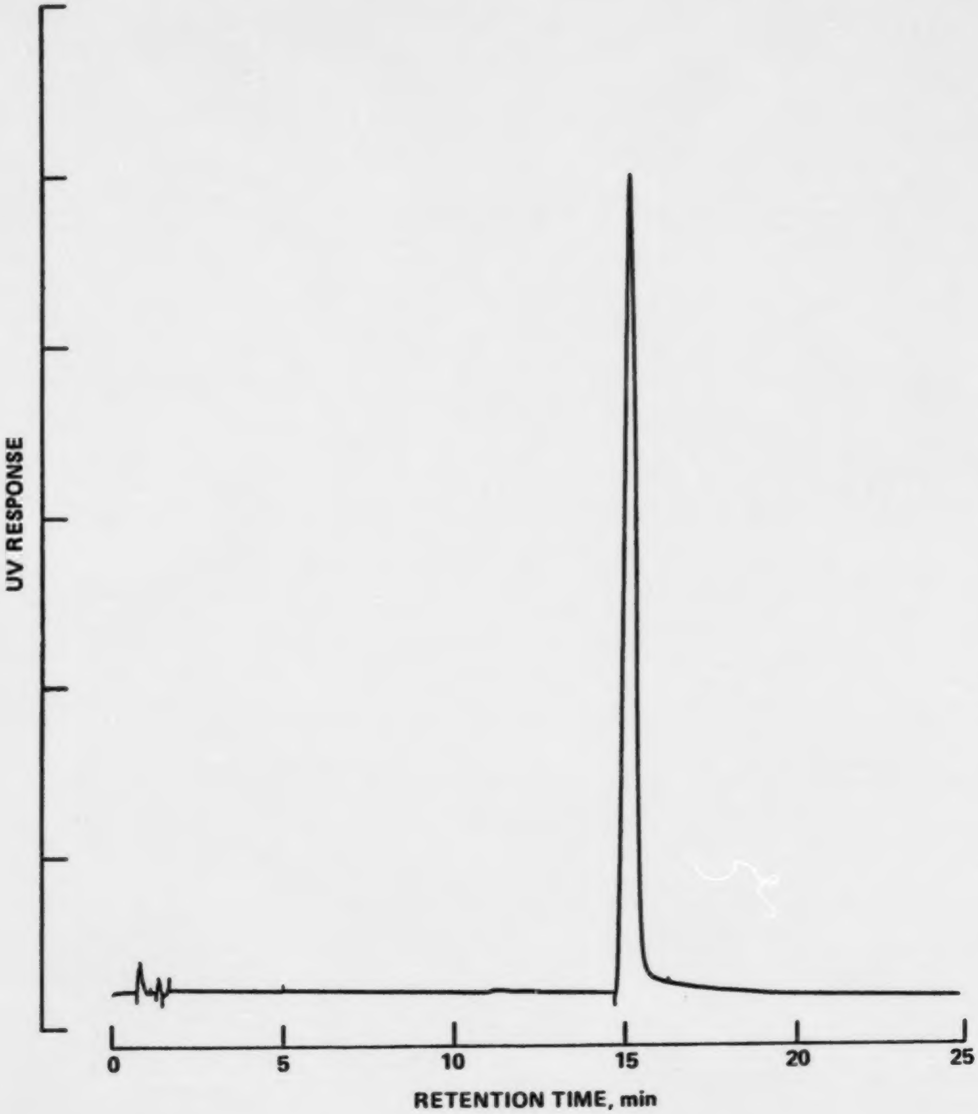


Figure C-4. Chromatogram by HPLC/UV for aflatoxin B-1.

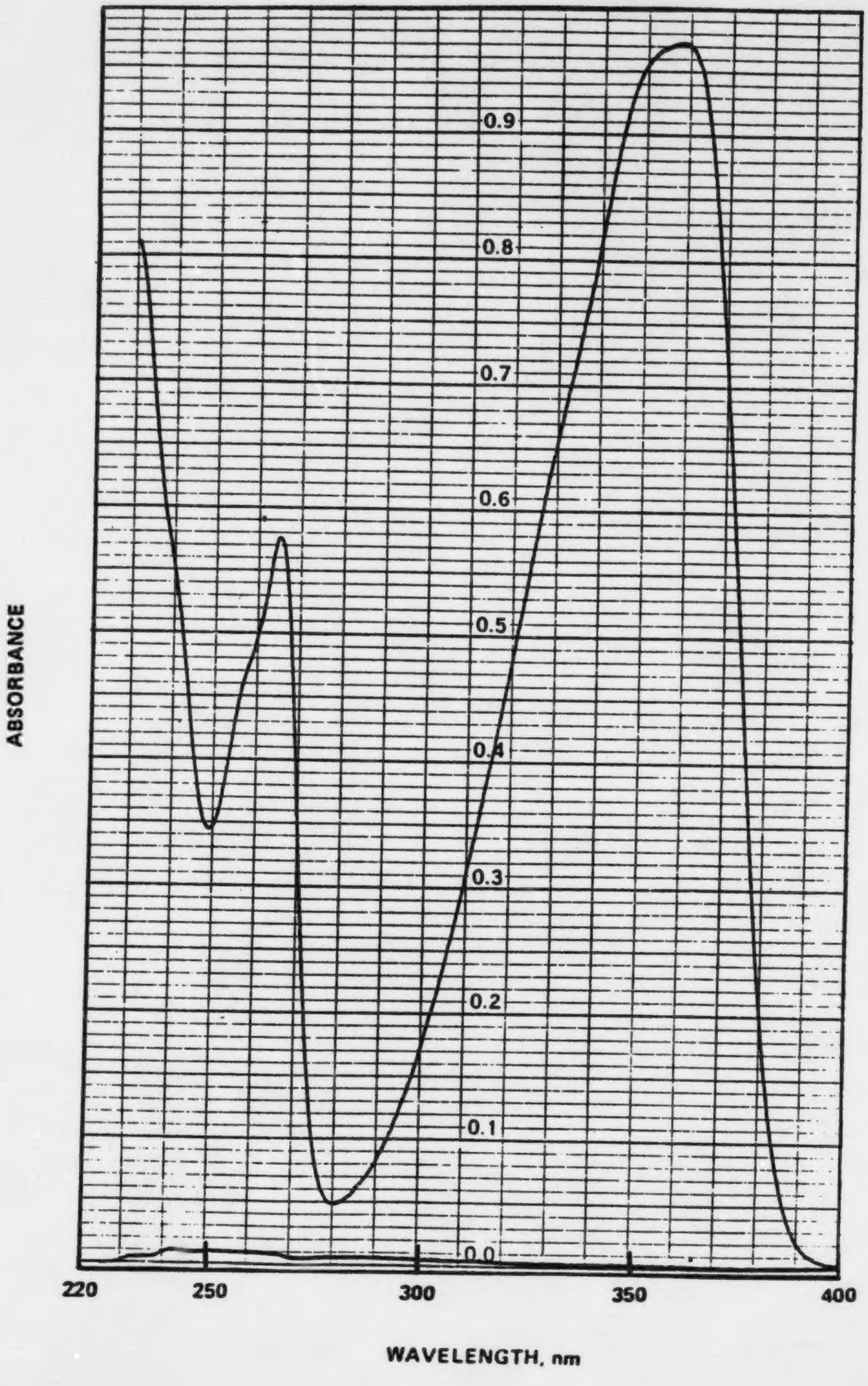


Figure C-5. UV spectrum of aflatoxin B-1.

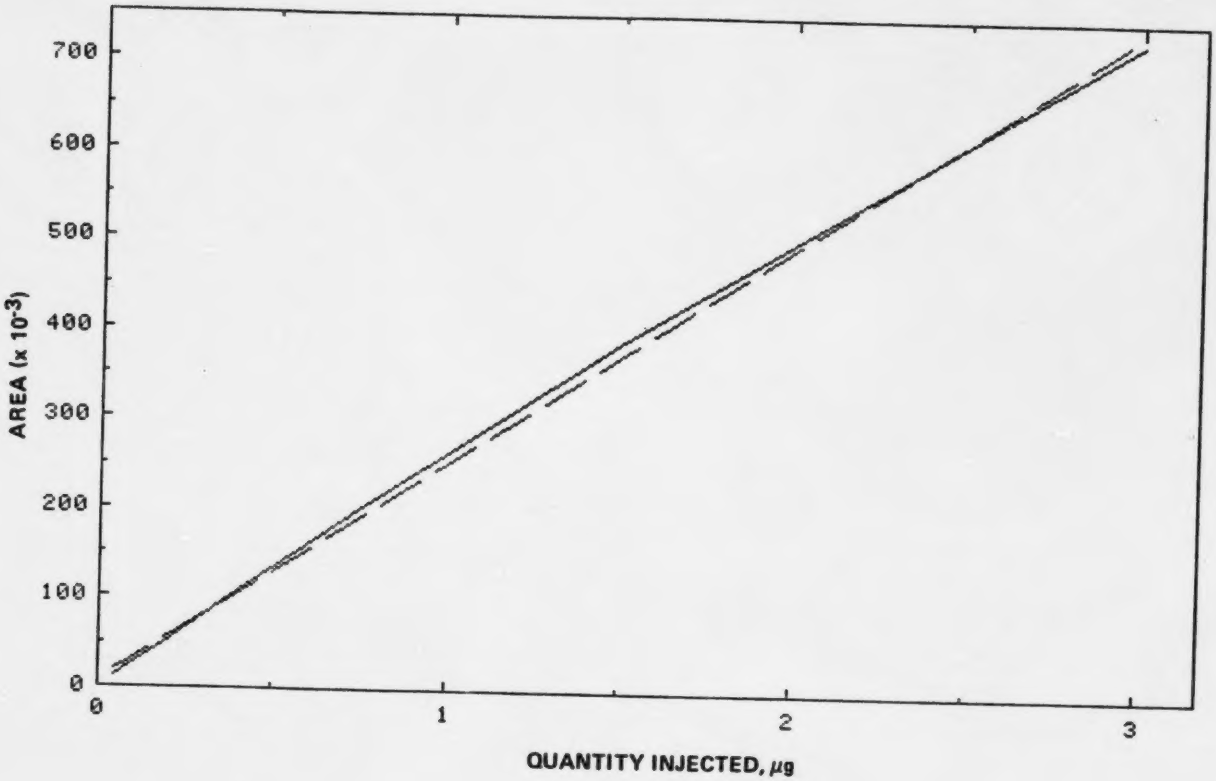


Figure C-6. Calibration curve for the determination of aflatoxin B-1 by HPLC/UV.

Range: 0.07-3 μg
Correlation coefficient: 0.999
Slope: 3.19×10^2
y-Intercept: 1.20×10^1

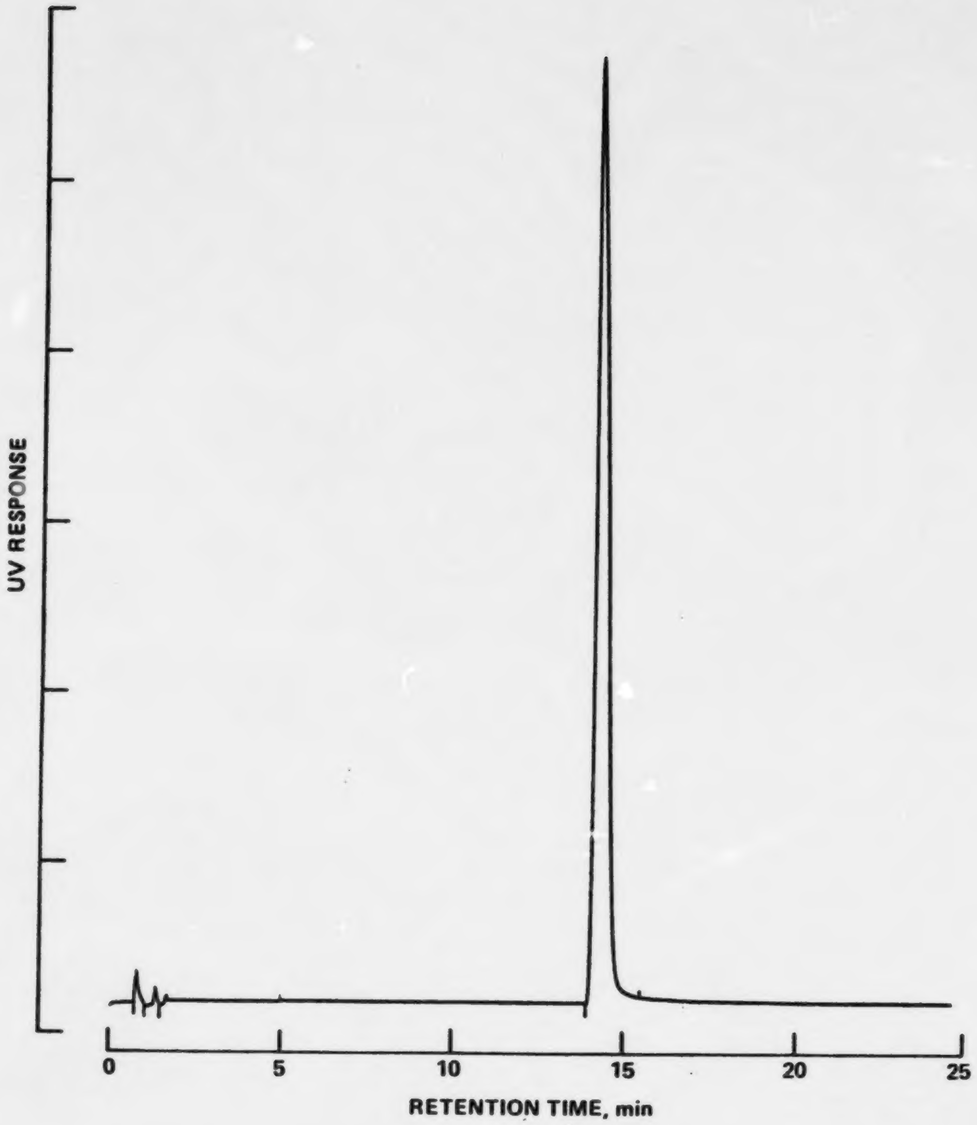


Figure C-7. Chromatogram by HPLC/UV for aflatoxin B-2.

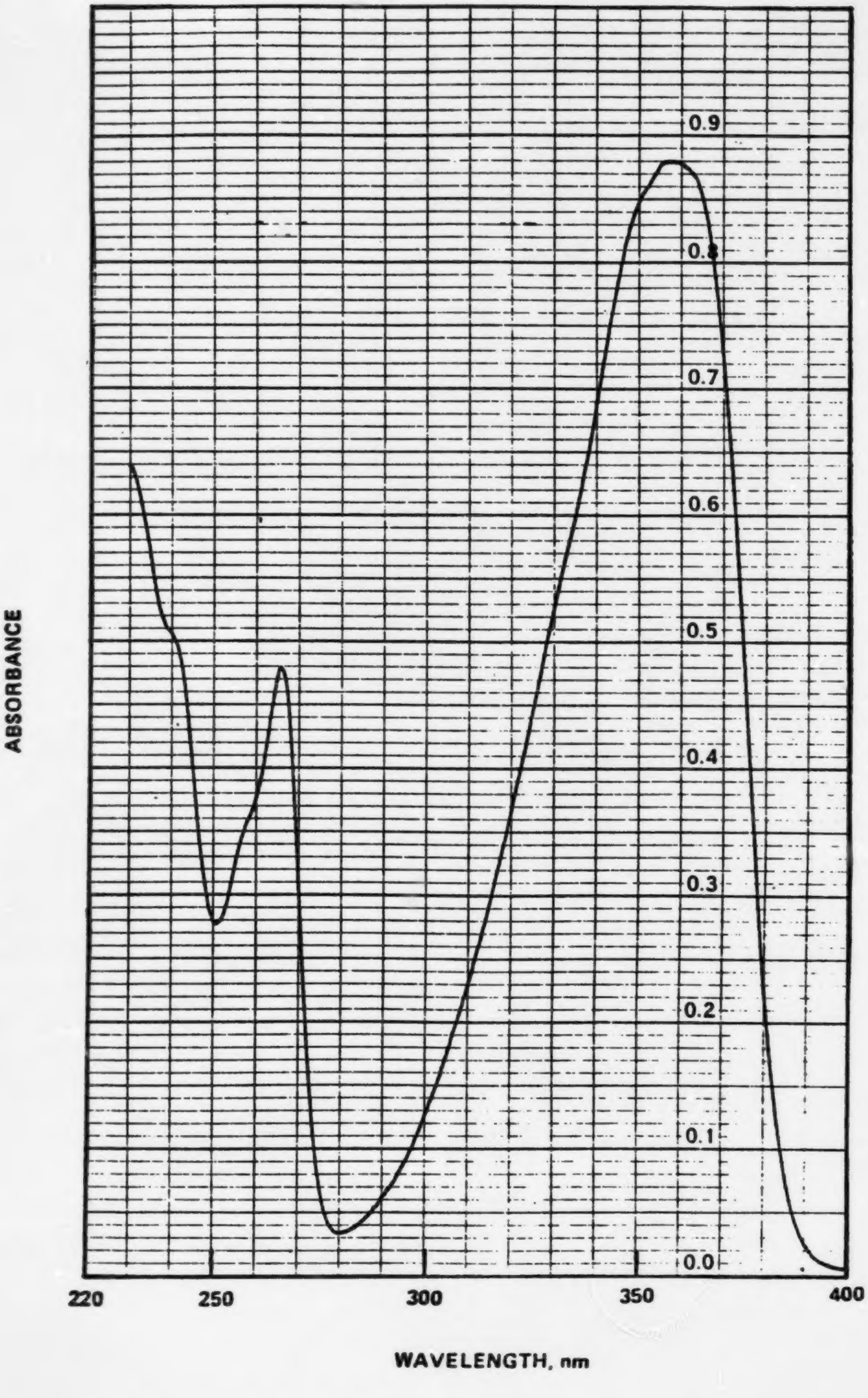


Figure C-8. UV spectrum of aflatoxin B-2.

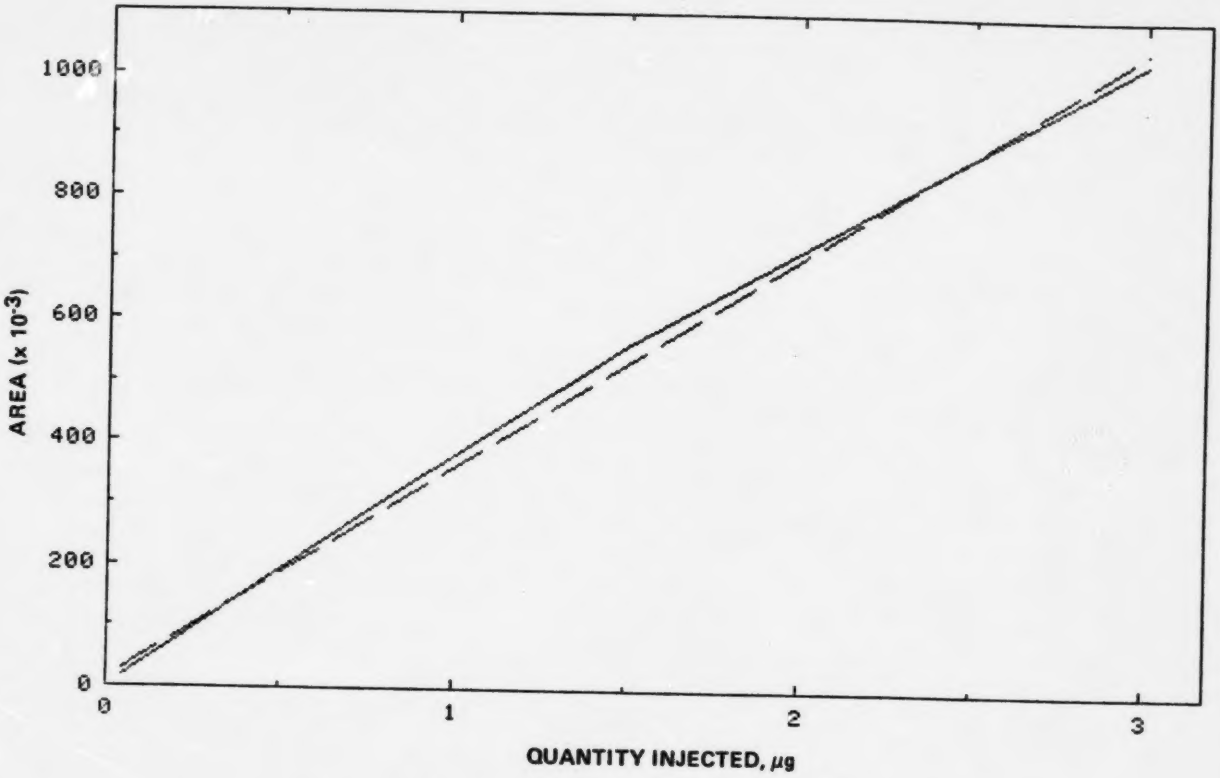


Figure C-9. Calibration curve for the determination of aflatoxin B-2 by HPLC/UV.

Range: 0.03-3 μg
Correlation coefficient: 0.999
Slope: 3.44×10^2
y-Intercept: 1.41×10^1

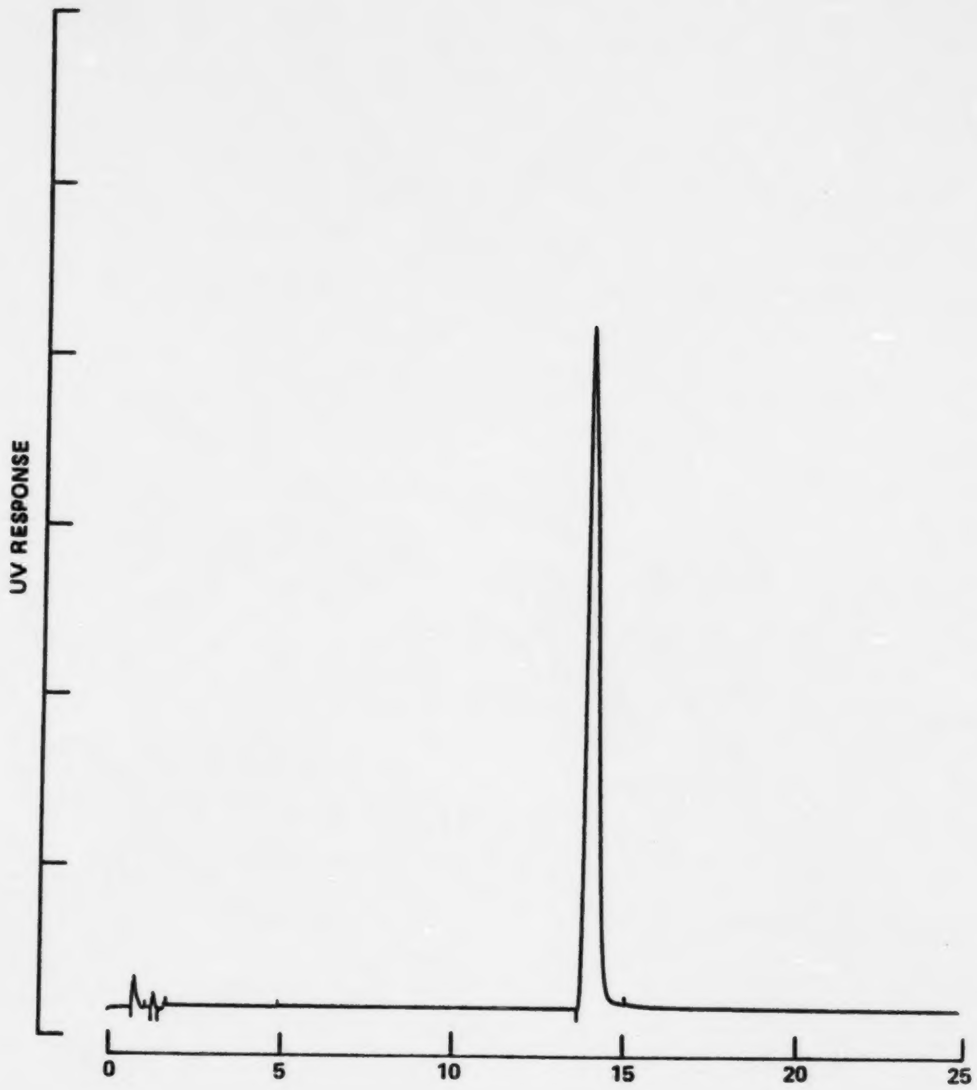


Figure C-10. Chromatogram by HPLC/UV for aflatoxin G-1.

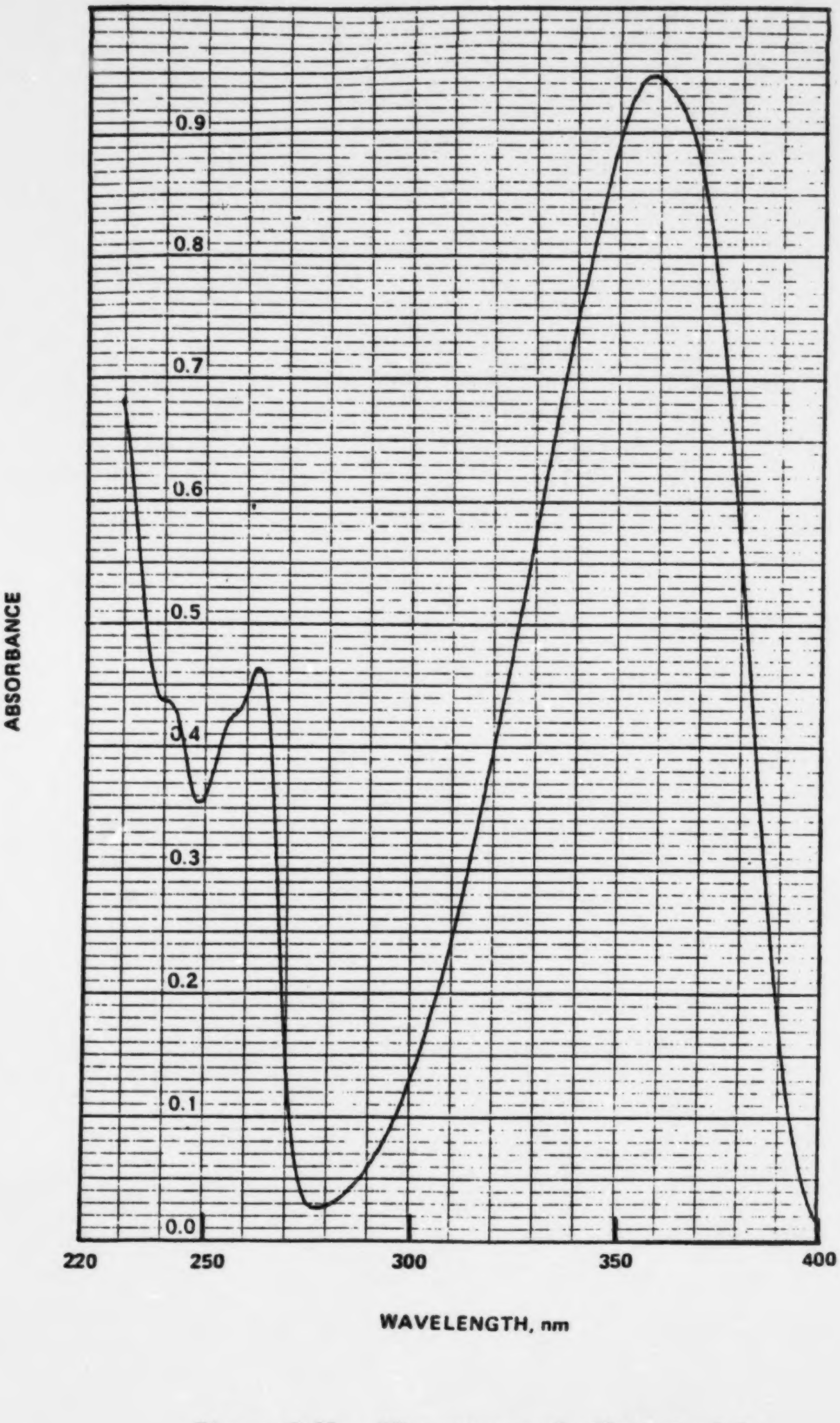


Figure C-11. UV spectrum of aflatoxin G-1.

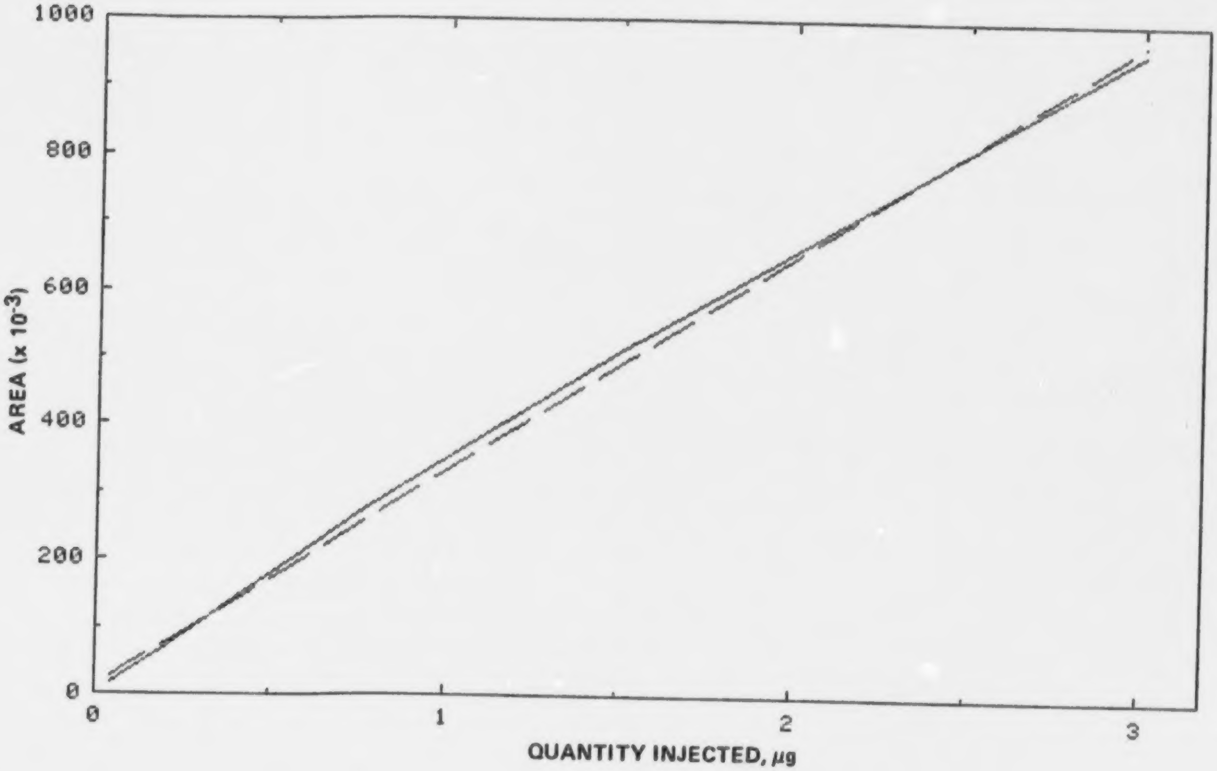


Figure C-12. Calibration curve for the determination of aflatoxin G-1 by HPLC/UV.

Range: 0.07-3 µg
Correlation coefficient: 0.999
Slope: 2.43×10^2
y-Intercept: 7.50

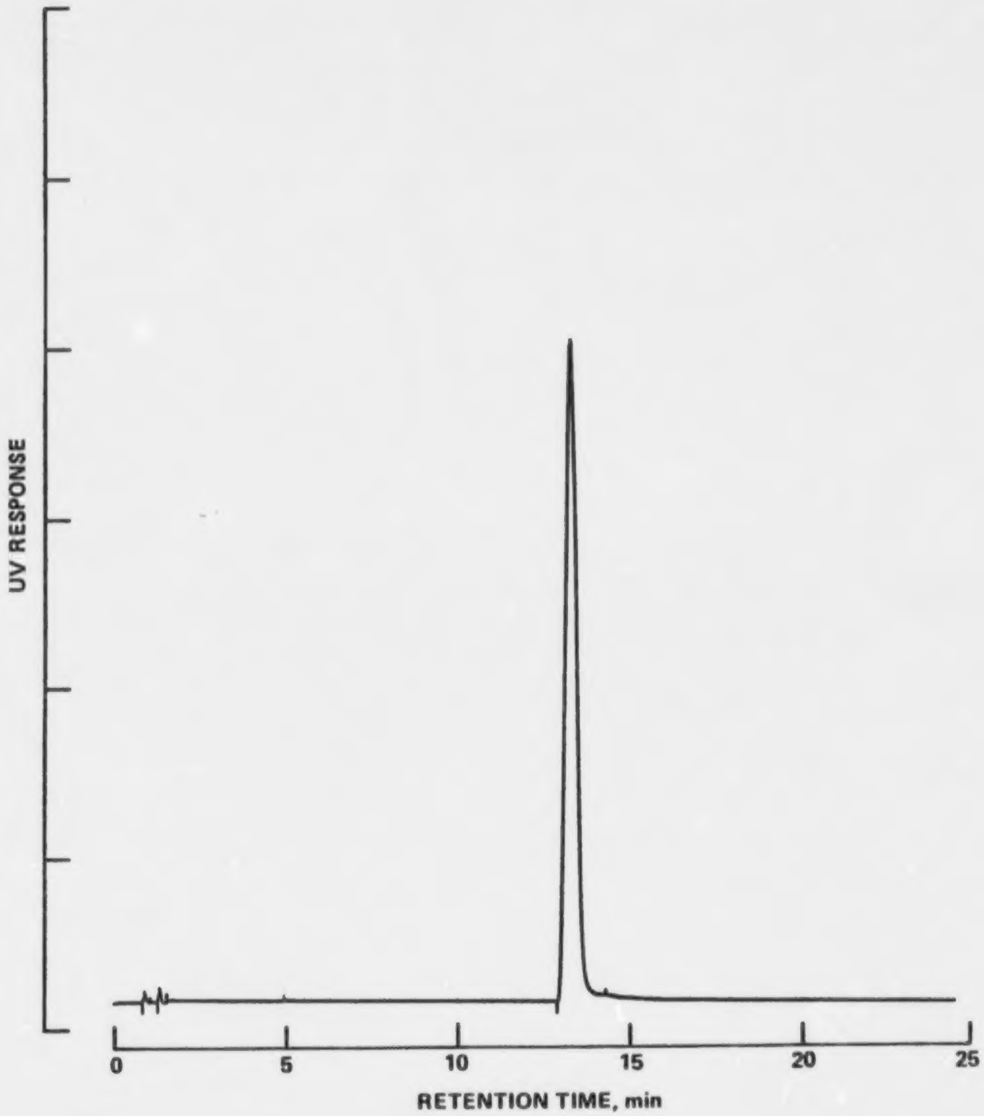


Figure C-13. Chromatogram by HPLC/UV for aflatoxin G-2.

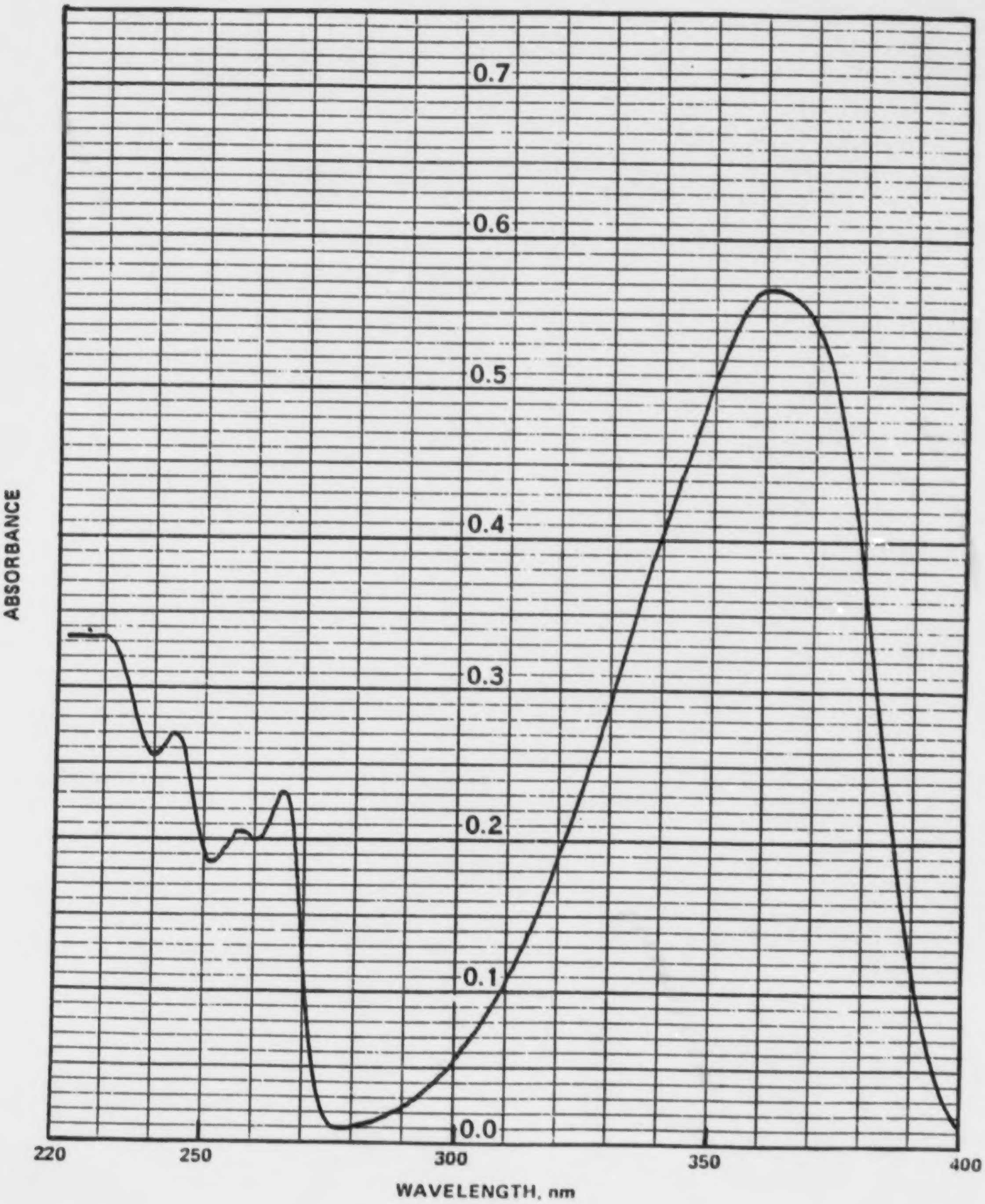


Figure C-14. UV spectrum of aflatoxin G-2.

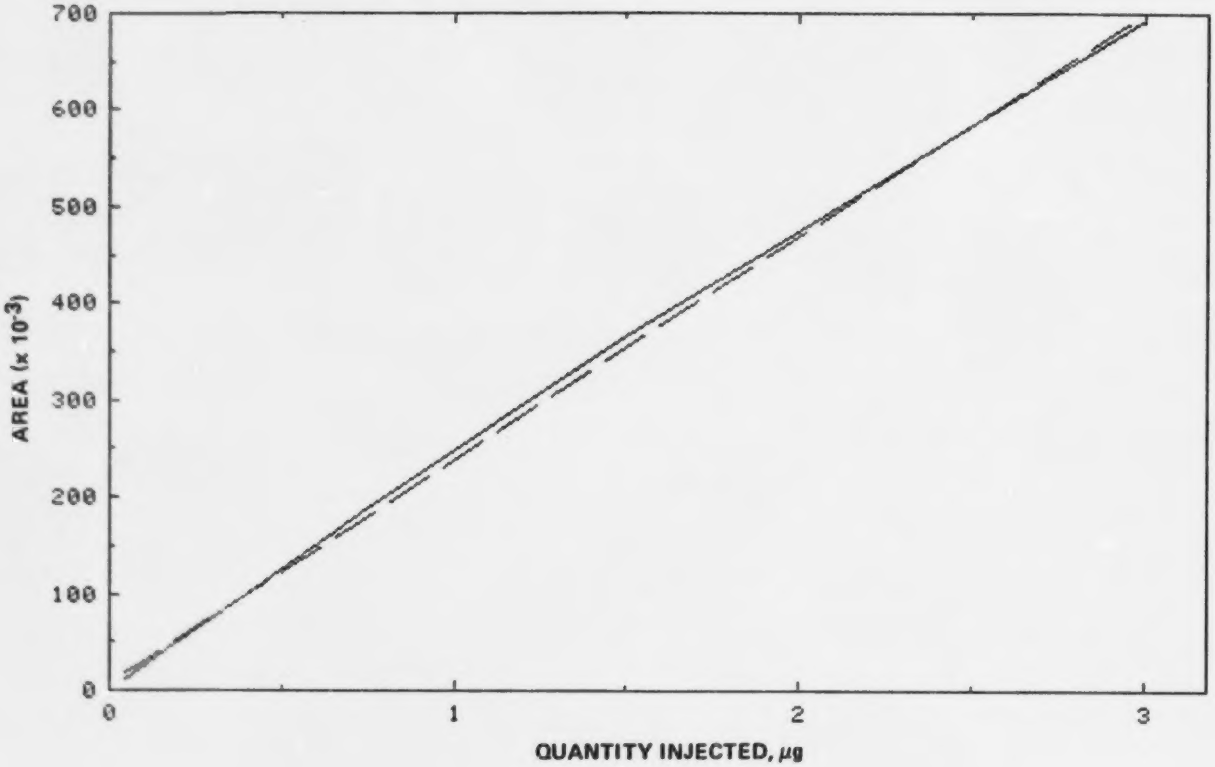


Figure C-15. Calibration curve for the determination of aflatoxin G-2 by HPLC/UV.

Range: 0.03-3 μg
Correlation coefficient: 0.999
Slope: 2.32×10^2
y-Intercept: 6.63

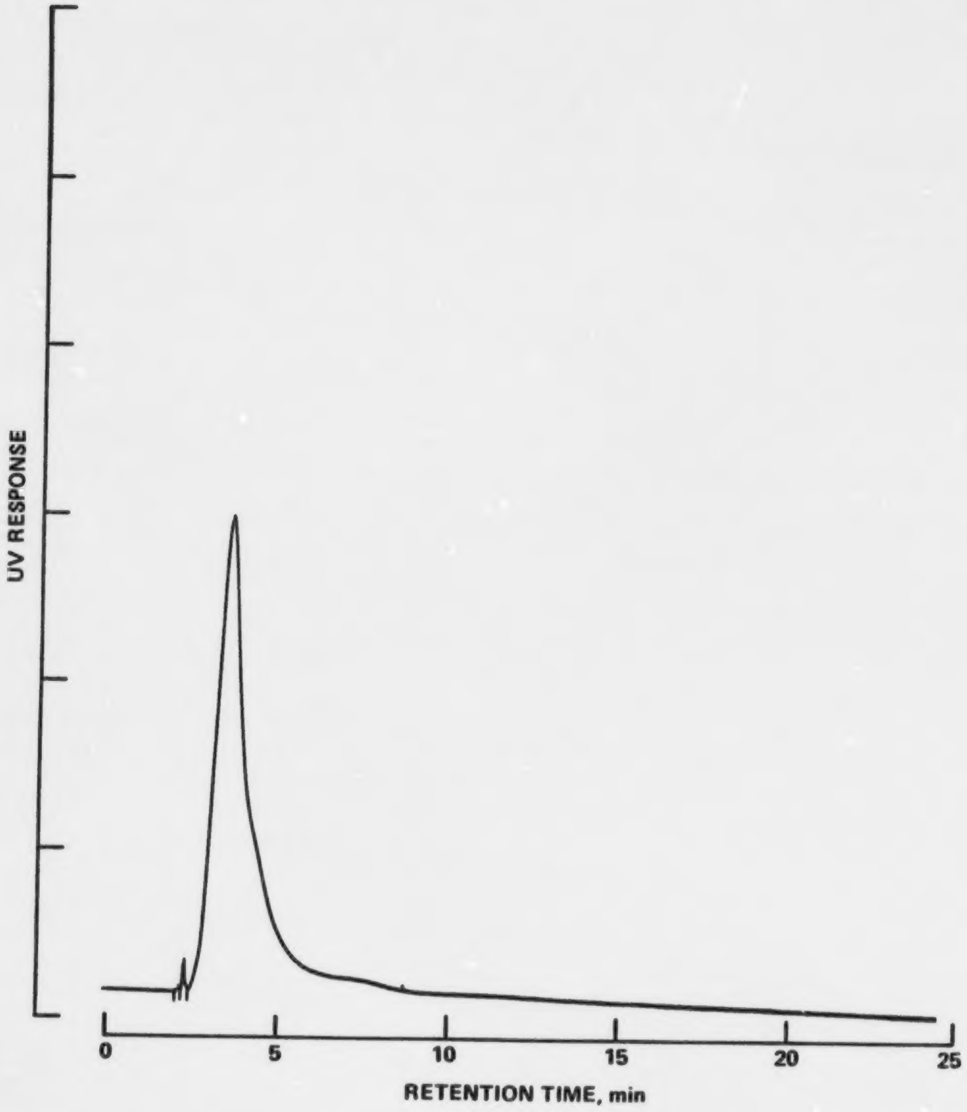


Figure C-16. Chromatogram by HPLC/UV for benzenearsonic acid.

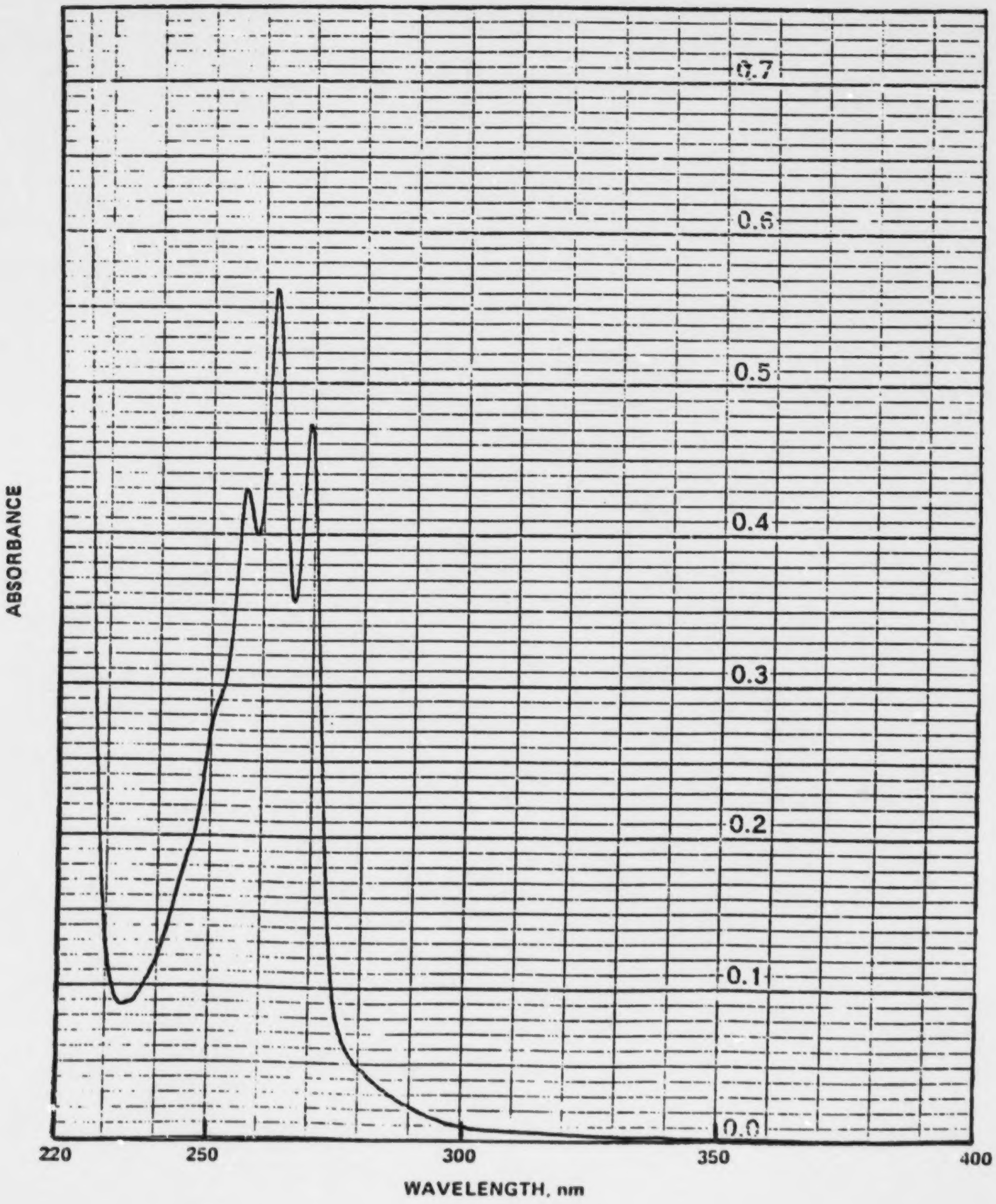


Figure C-17. UV spectrum of benzenearsonic acid.

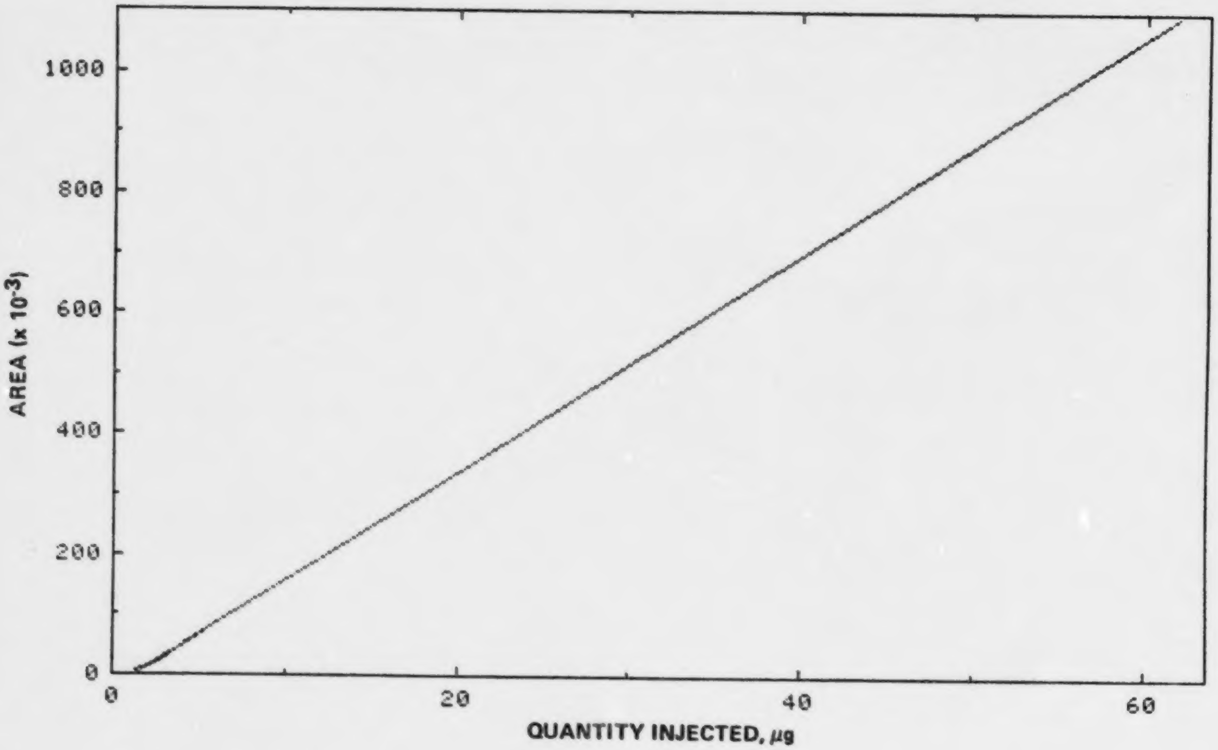


Figure C-18. Calibration curve for the determination of benzenearsonic acid by HPLC/UV.

Range: 6-60 μg
Correlation coefficient: 0.999
Slope: 1.80×10^1
y-Intercept: -2.23×10^1

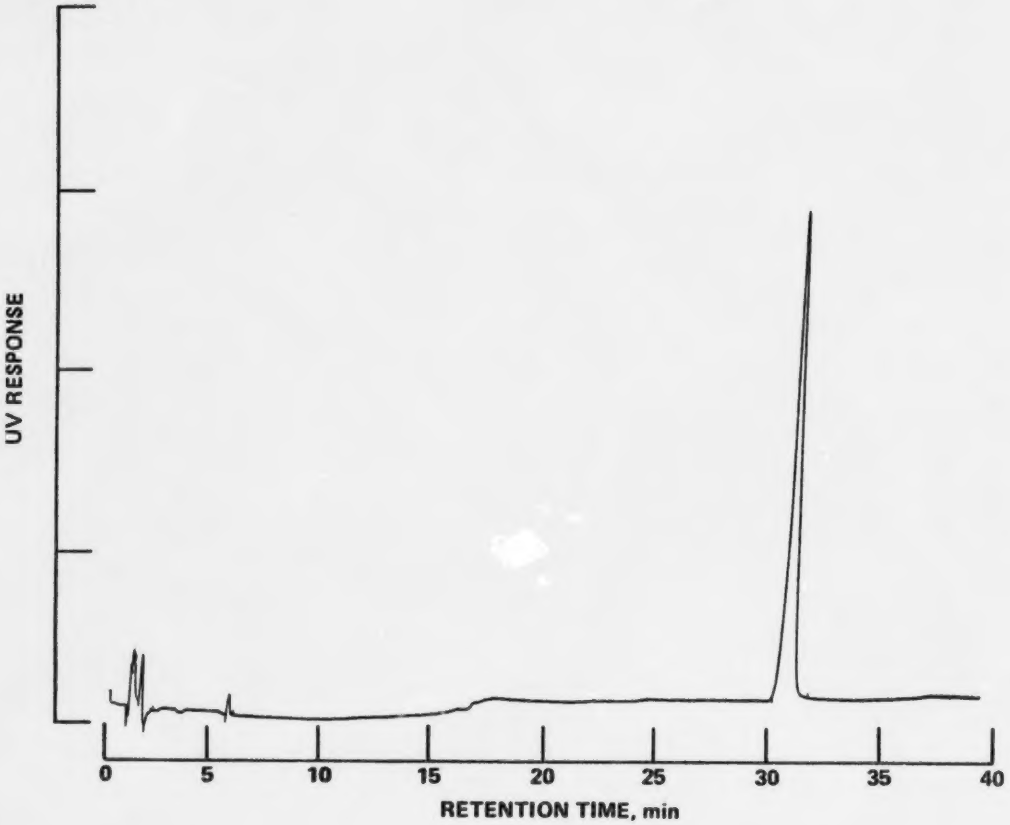


Figure C-19. Chromatogram by HPLC/UV for benz(a)anthracene.

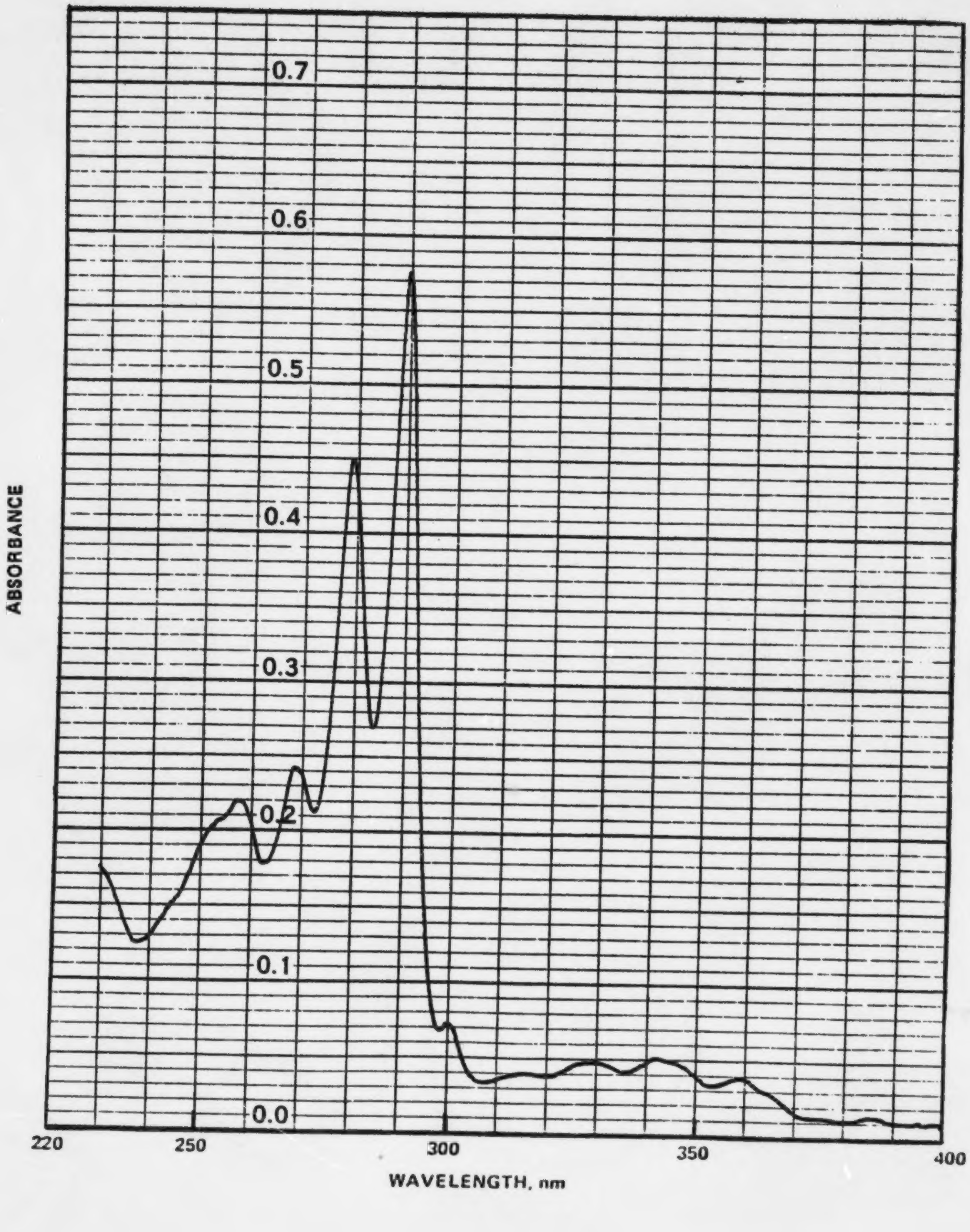


Figure C-20. UV spectrum of benz(a)anthracene.

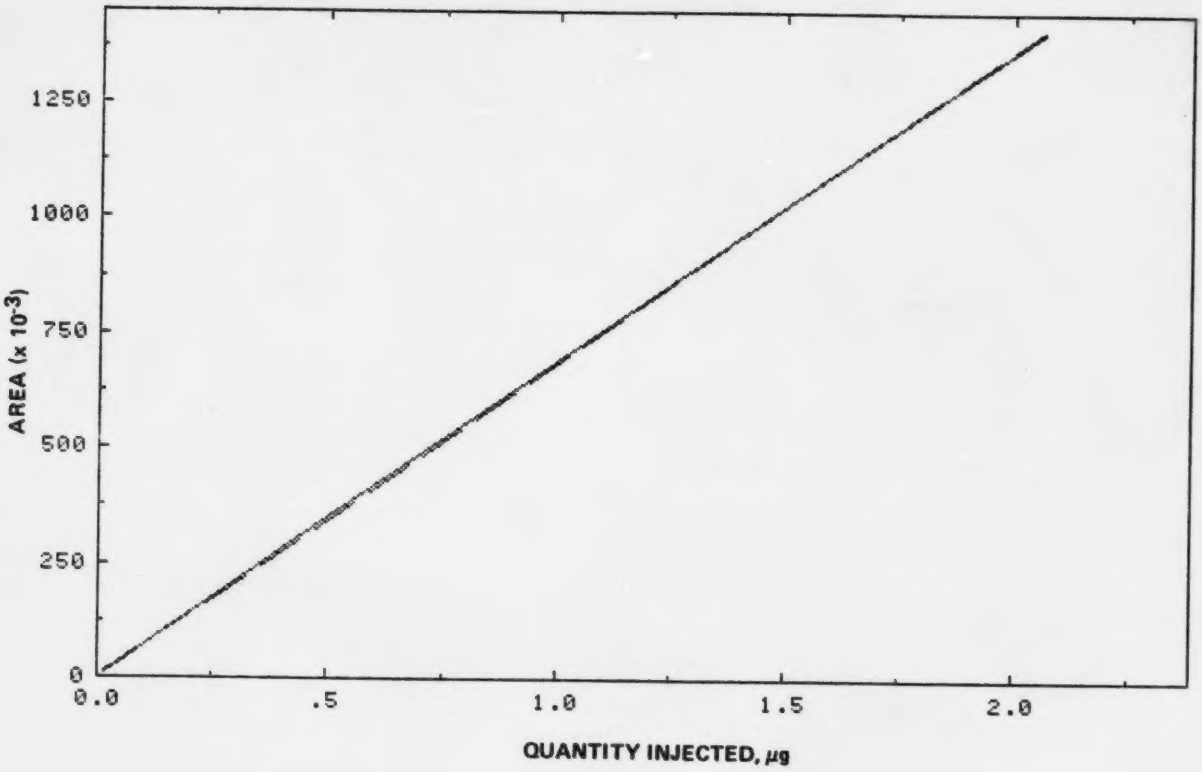


Figure C-21. Calibration curve for the determination of benz(a)anthracene by HPLC/UV.

Range: 0.02-2 µg
Correlation coefficient: 0.999
Slope: 6.82×10^2
y-Intercept: 2.96

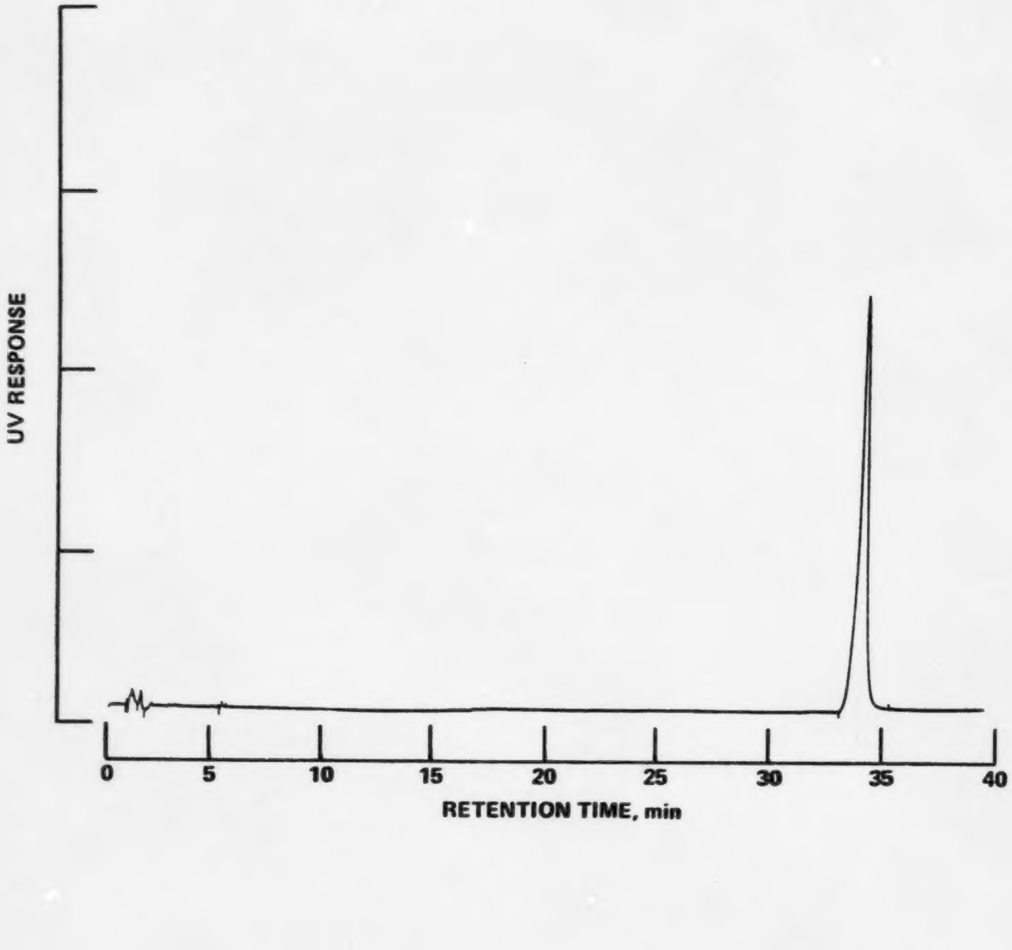


Figure C-22. Chromatogram by HPLC/UV for benzo(b)fluoranthene.

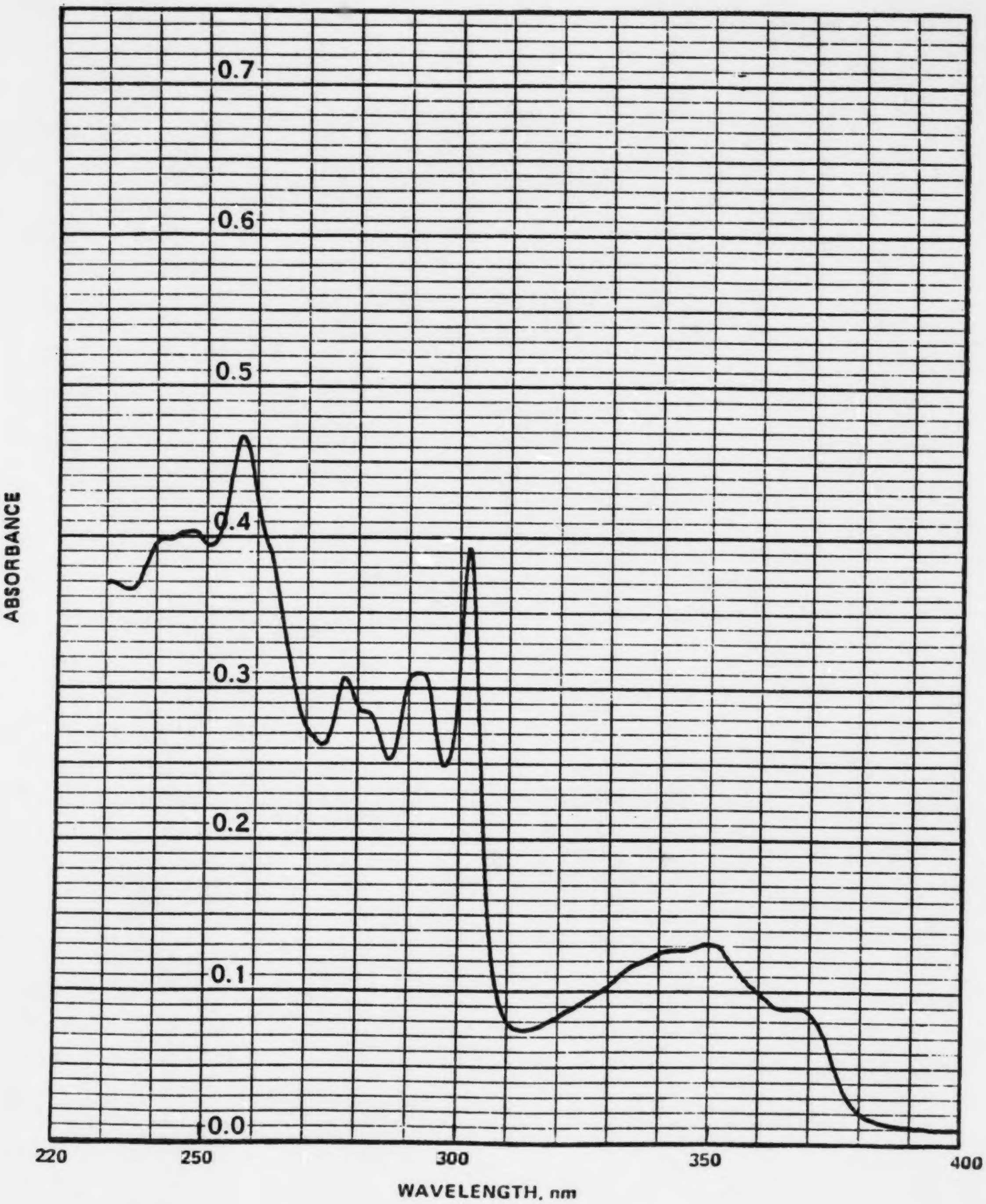


Figure C-23. UV spectrum of benzo(b)fluoranthene.

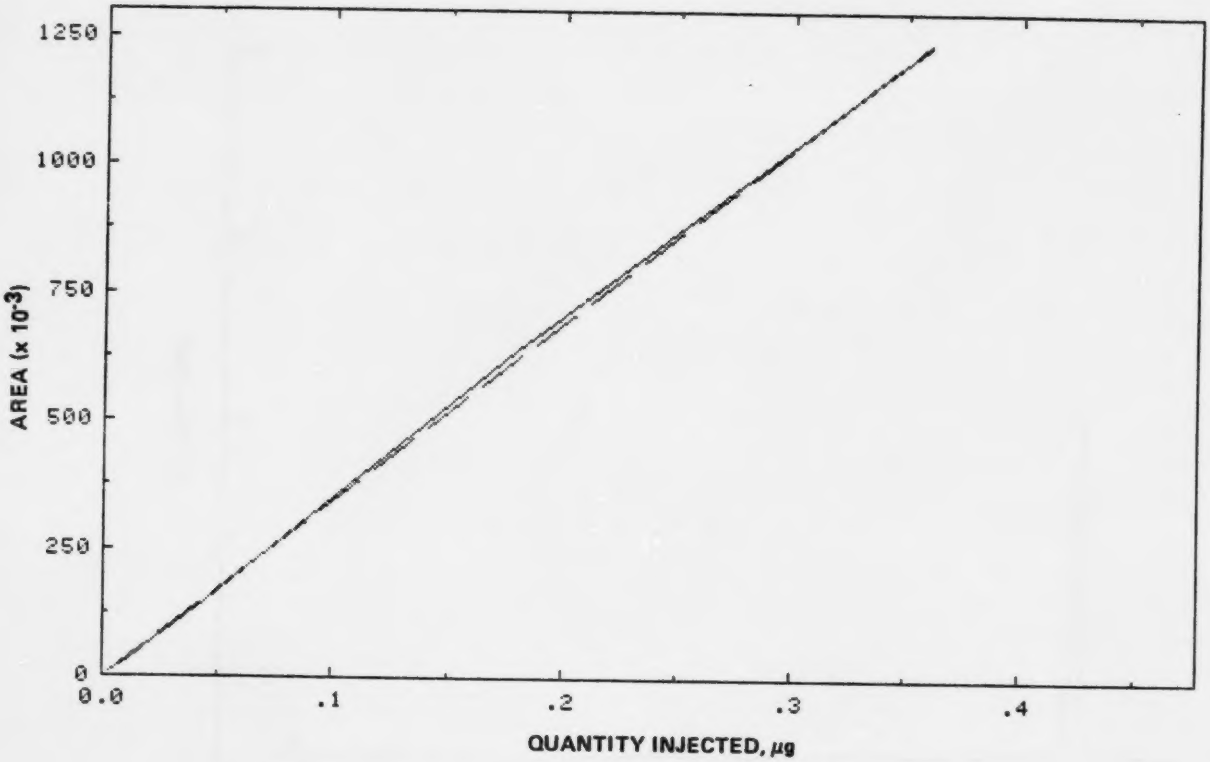


Figure C-24. Calibration curve for the determination of benzo(b)fluoranthene by HPLC/UV.

Range: 0.001-0.360 µg
Correlation coefficient: 0.999
Slope: 3.45×10^3
y-Intercept: -9.08×10^{-1}

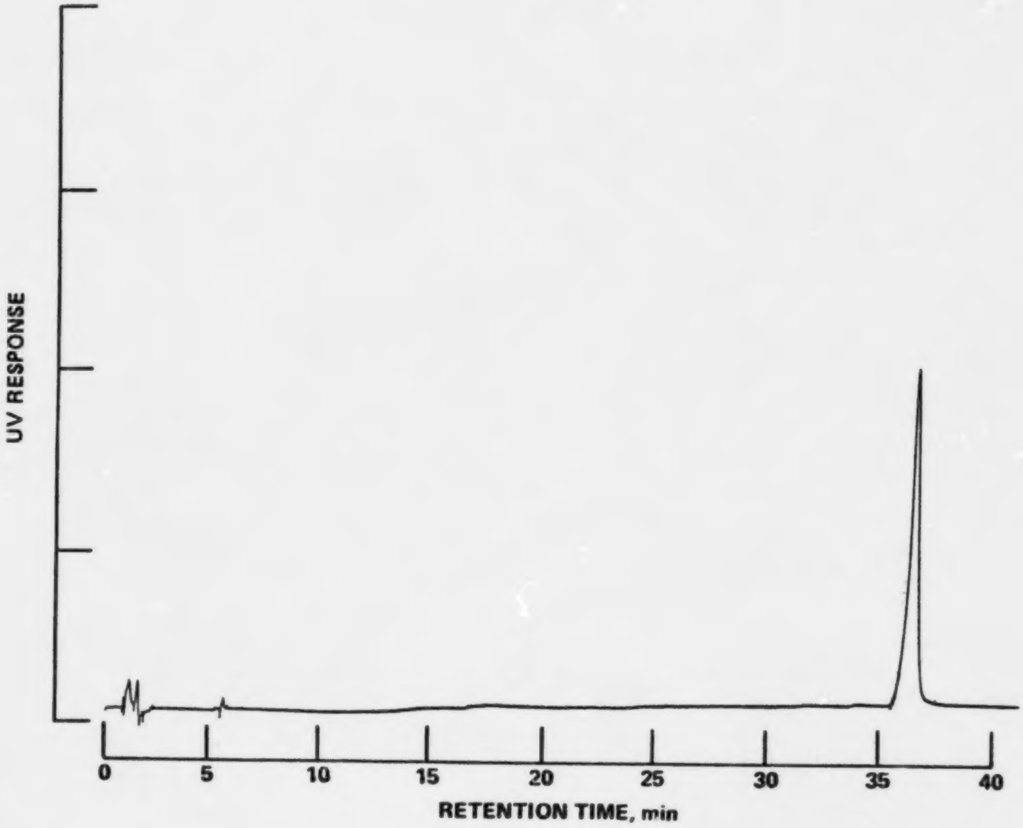


Figure C-25. Chromatogram by HPLC/UV for benzo(a)pyrene.

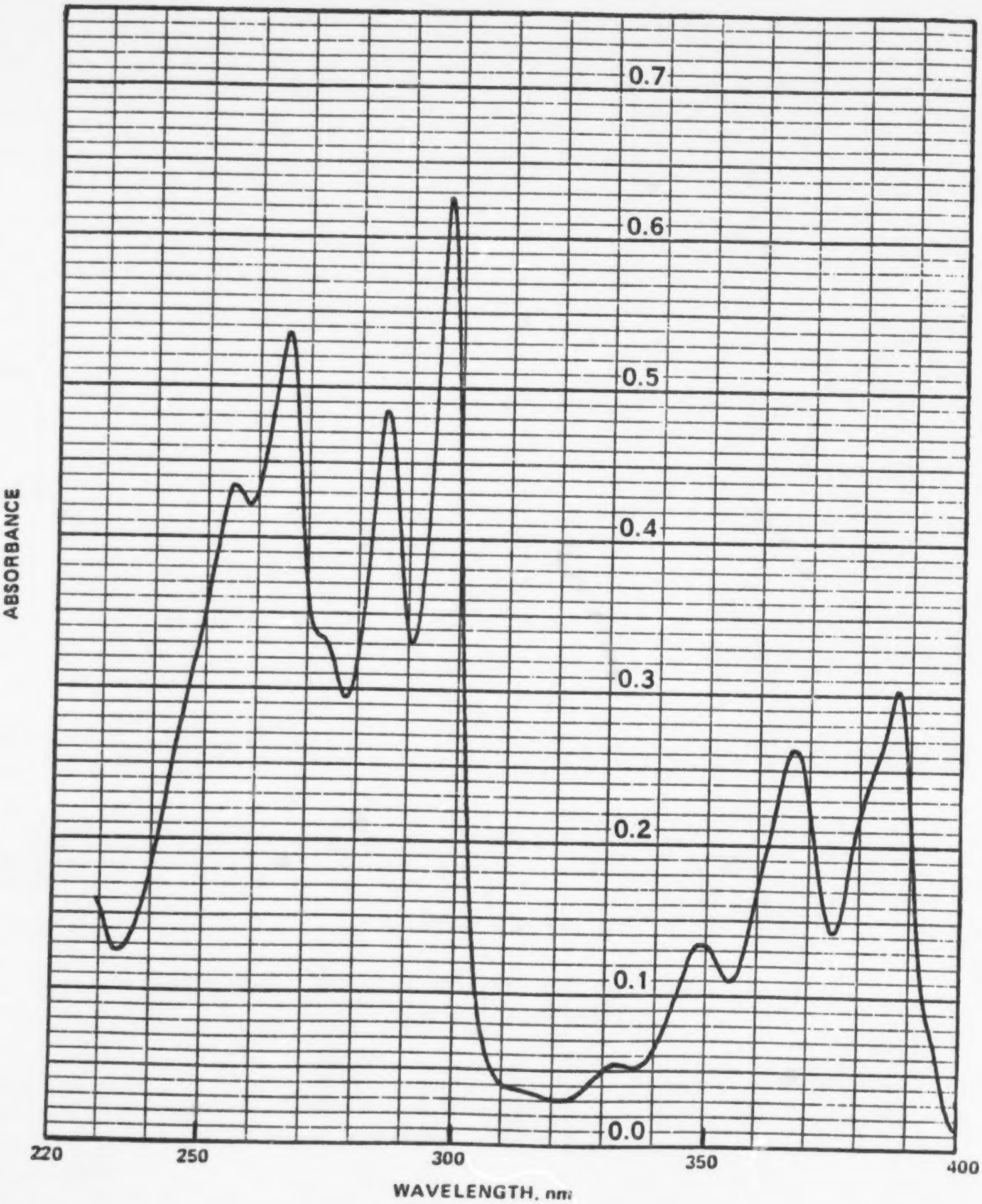


Figure C-26. UV spectrum of benzo(a)pyrene.

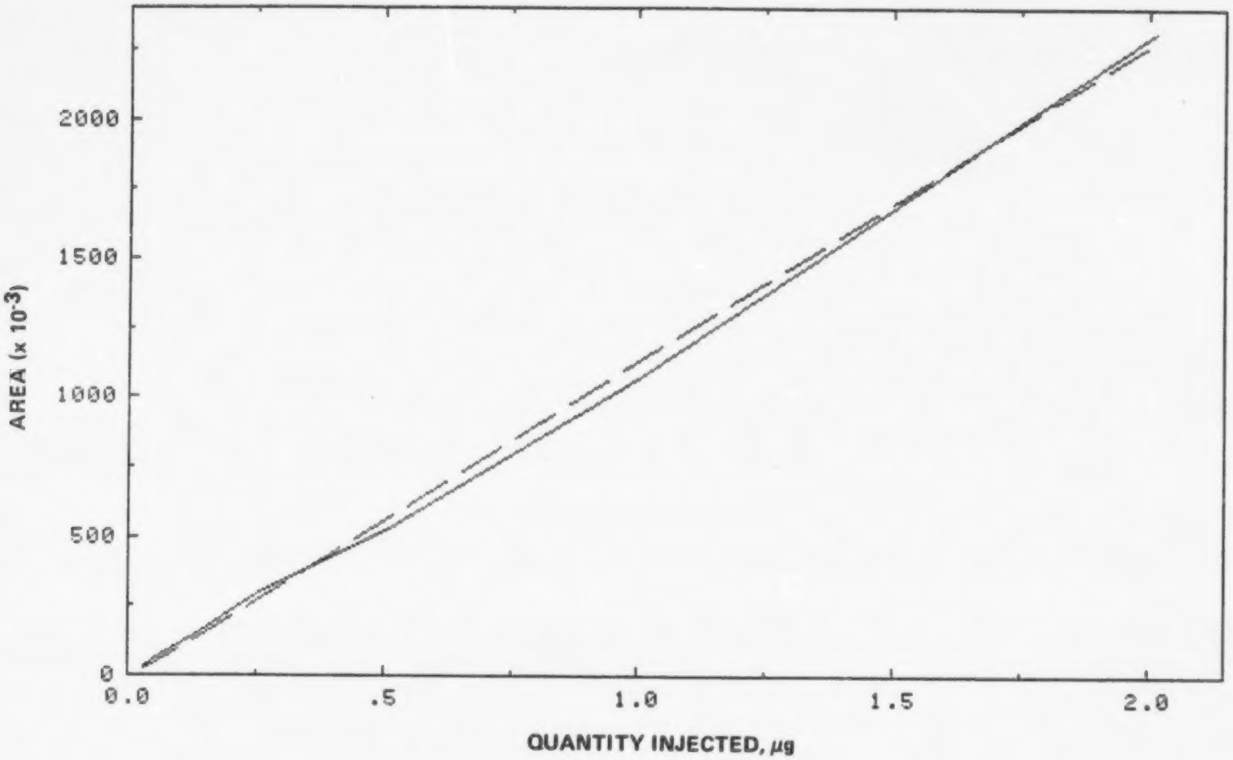


Figure C-27. Calibration curve for the determination of benzo(a)pyrene by HPLC/UV.

Range: 0.02-2 μg
Correlation coefficient: 0.999
Slope: 1.34×10^3
y-Intercept: -1.48×10^1

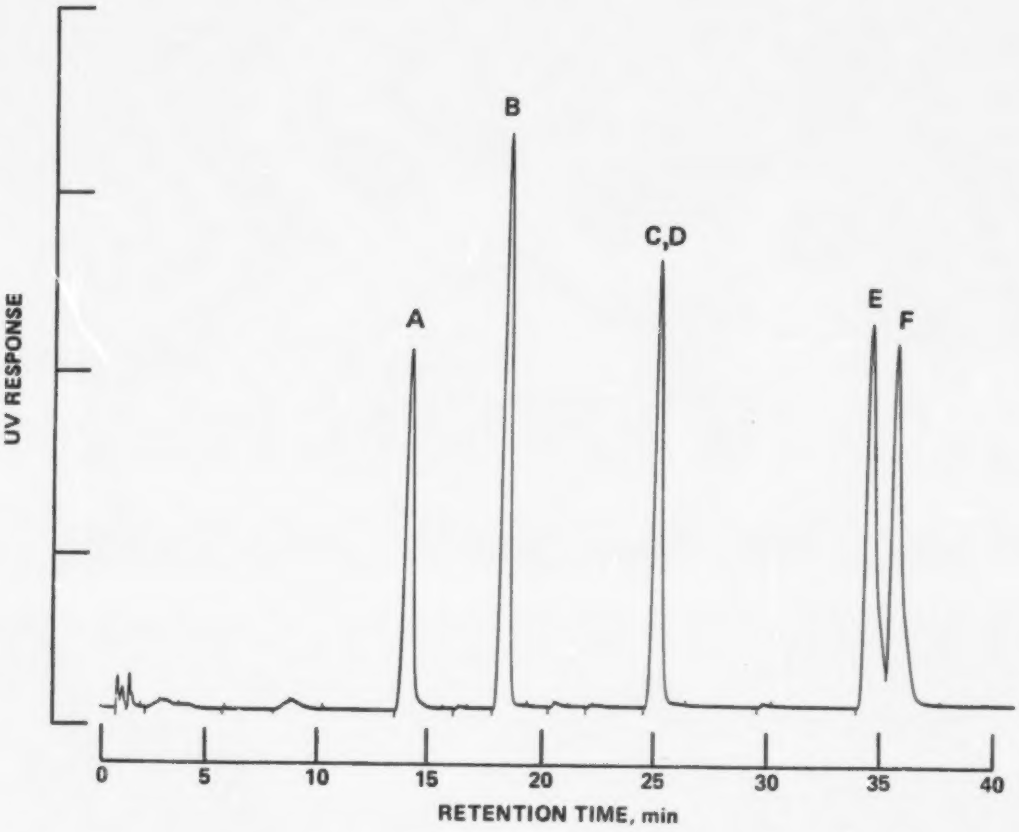


Figure C-28. Chromatogram by HPLC/UV: (A) dimethyl phthalate, (B) diethyl phthalate, (C) butyl benzyl phthalate, (D) di-n-butyl phthalate, (E) bis(2-ethylhexyl) phthalate, and (F) di-n-octyl phthalate.

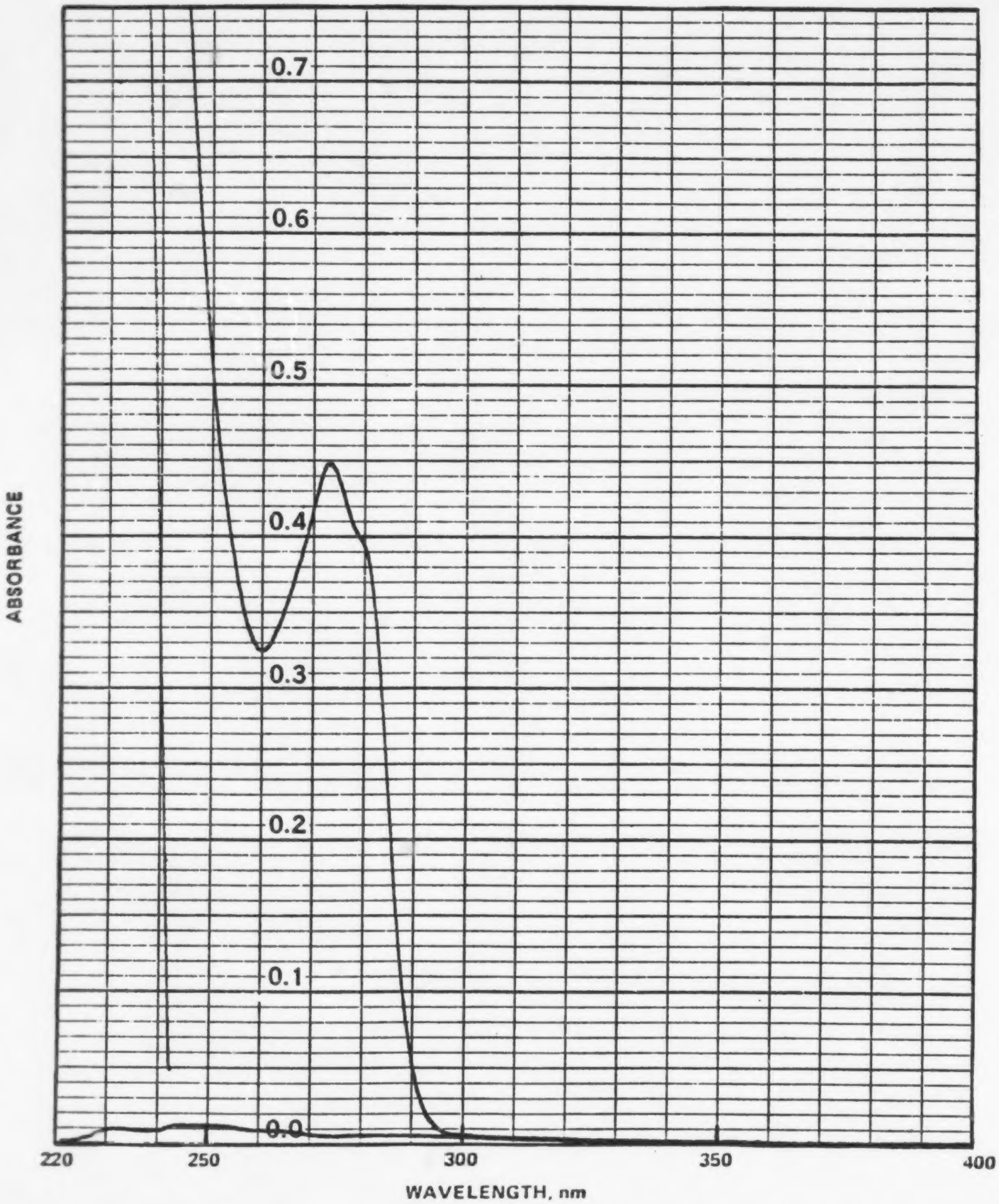


Figure C-29. UV spectrum of dimethyl phthalate.

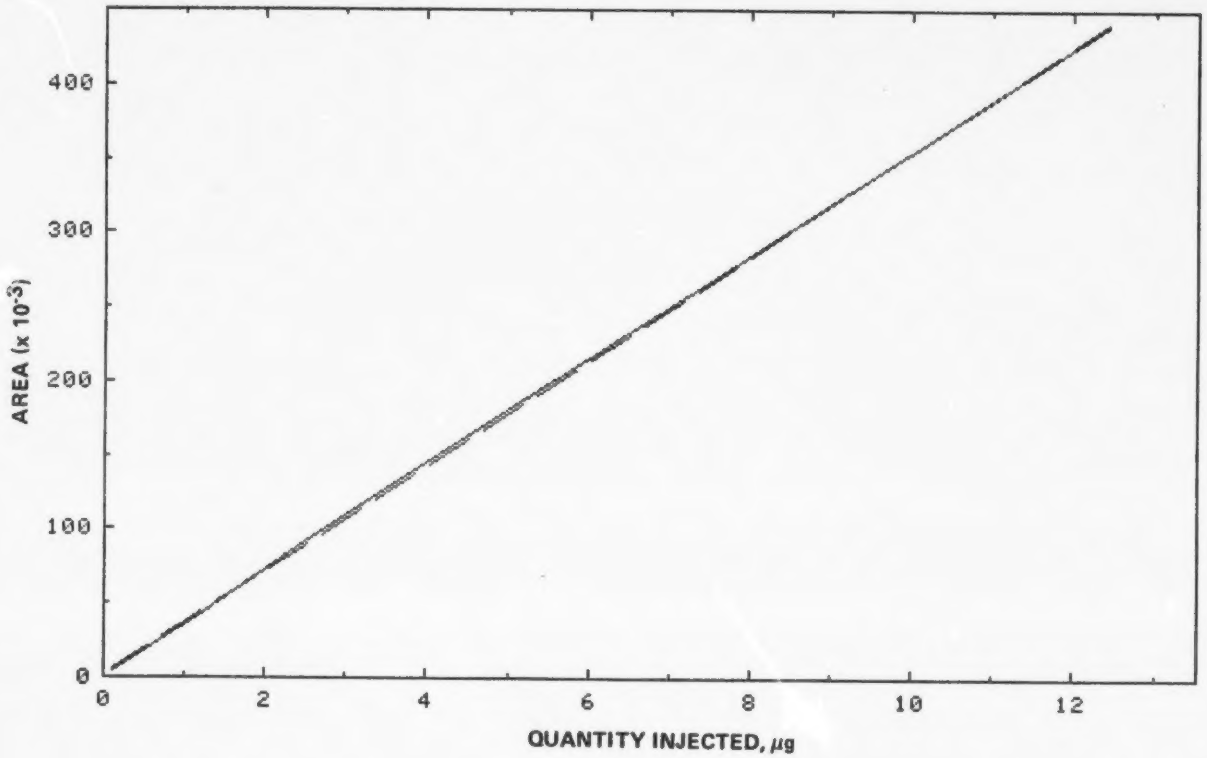


Figure C-30. Calibration curve for the determination of dimethyl phthalate by HPLC/UV.

Range: 0.1-10 µg
Correlation coefficient: 0.999
Slope: 3.54×10^1
y-Intercept: 1.470

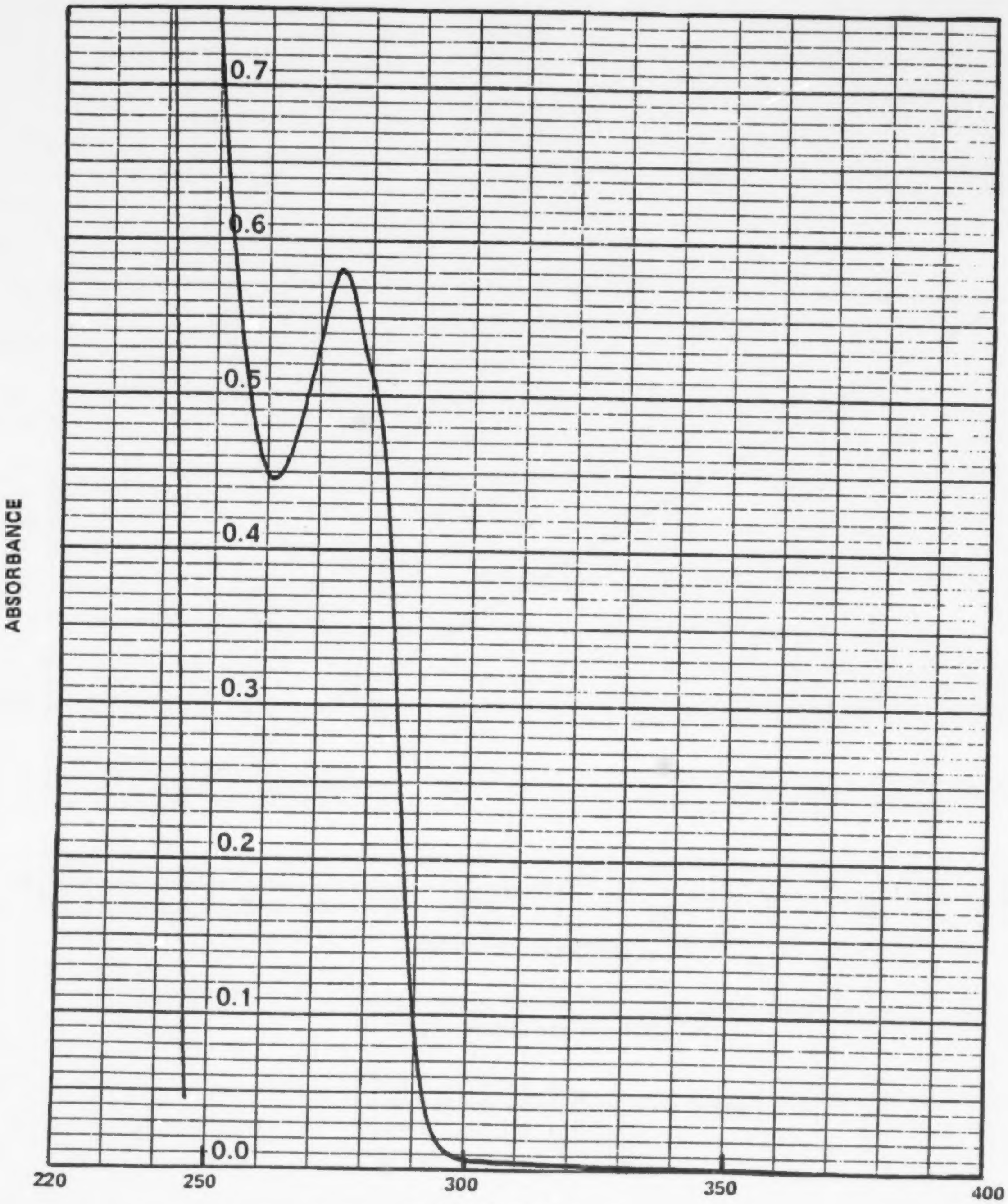


Figure C-31. UV spectrum of diethyl phthalate.

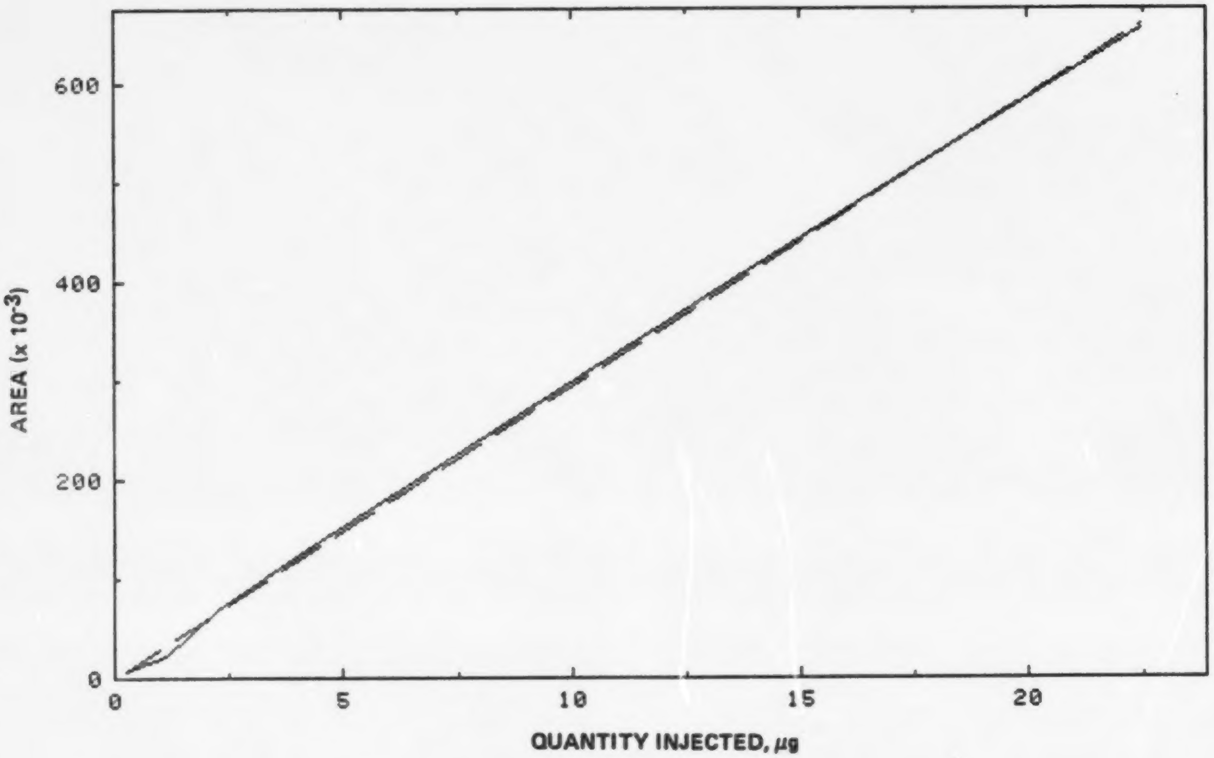


Figure C-32. Calibration curve for the determination of diethyl phthalate by HPLC/UV.

Range: 0.2-20 μg
Correlation coefficient: 0.999
Slope: 2.93×10^1
y-Intercept: 3.82×10^{-1}

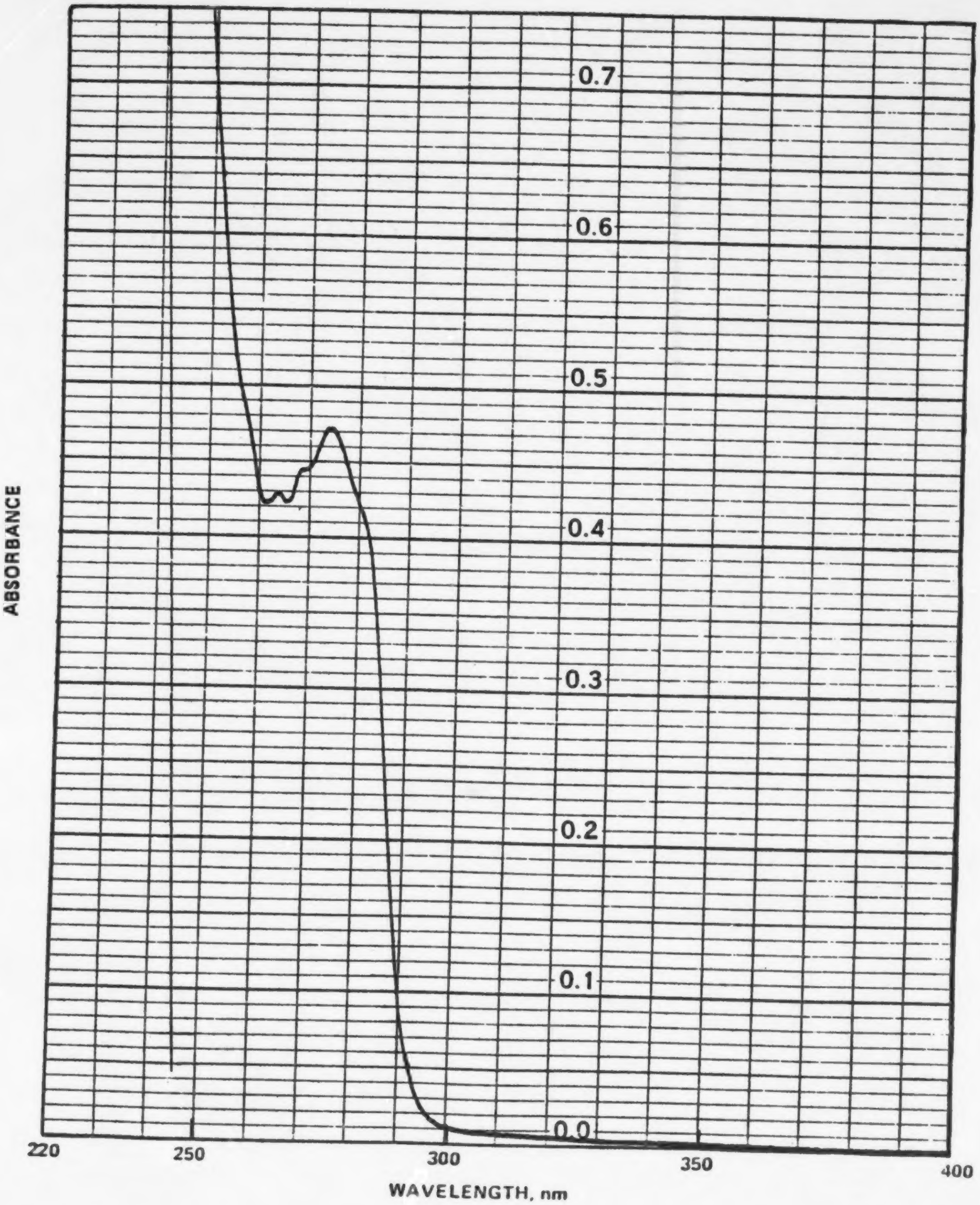


Figure C-33. UV spectrum of butyl benzyl phthalate.

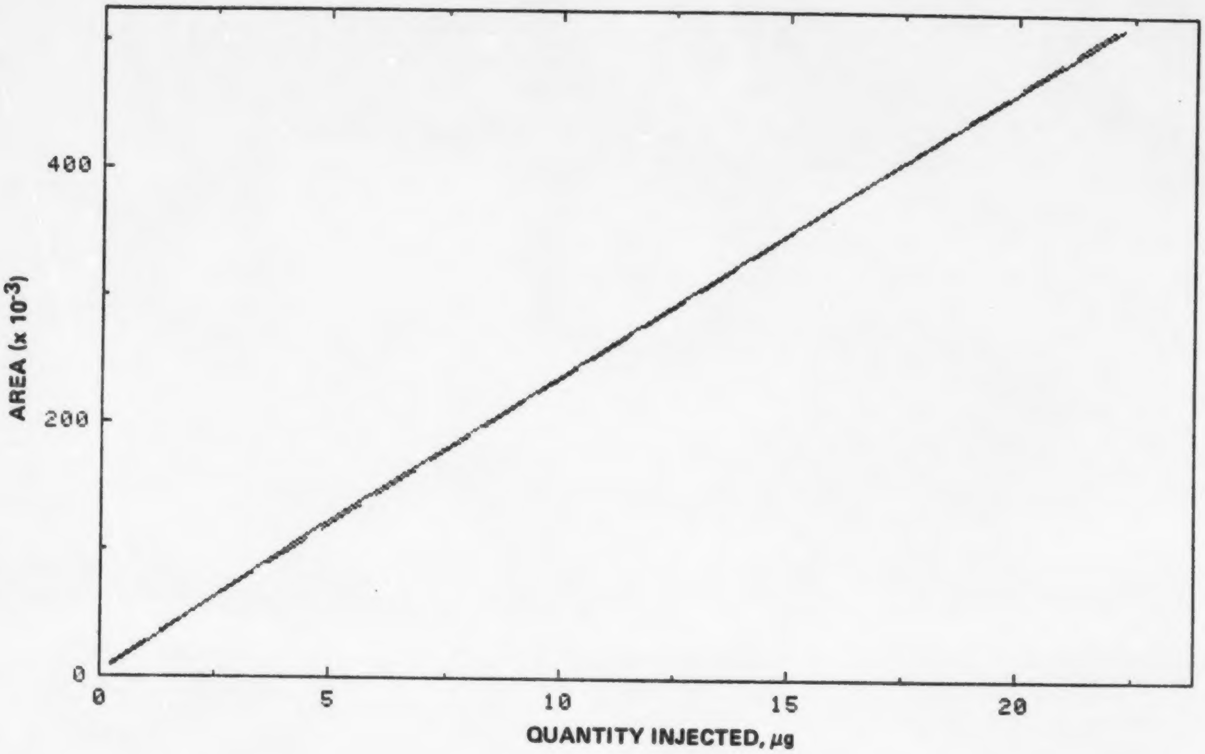


Figure C-34. Calibration curve for the determination of butyl benzyl phthalate by HPLC/UV.

Range: 0.2-20 µg
Correlation coefficient: 0.999
Slope: 2.30×10^1
y-Intercept: 5.53

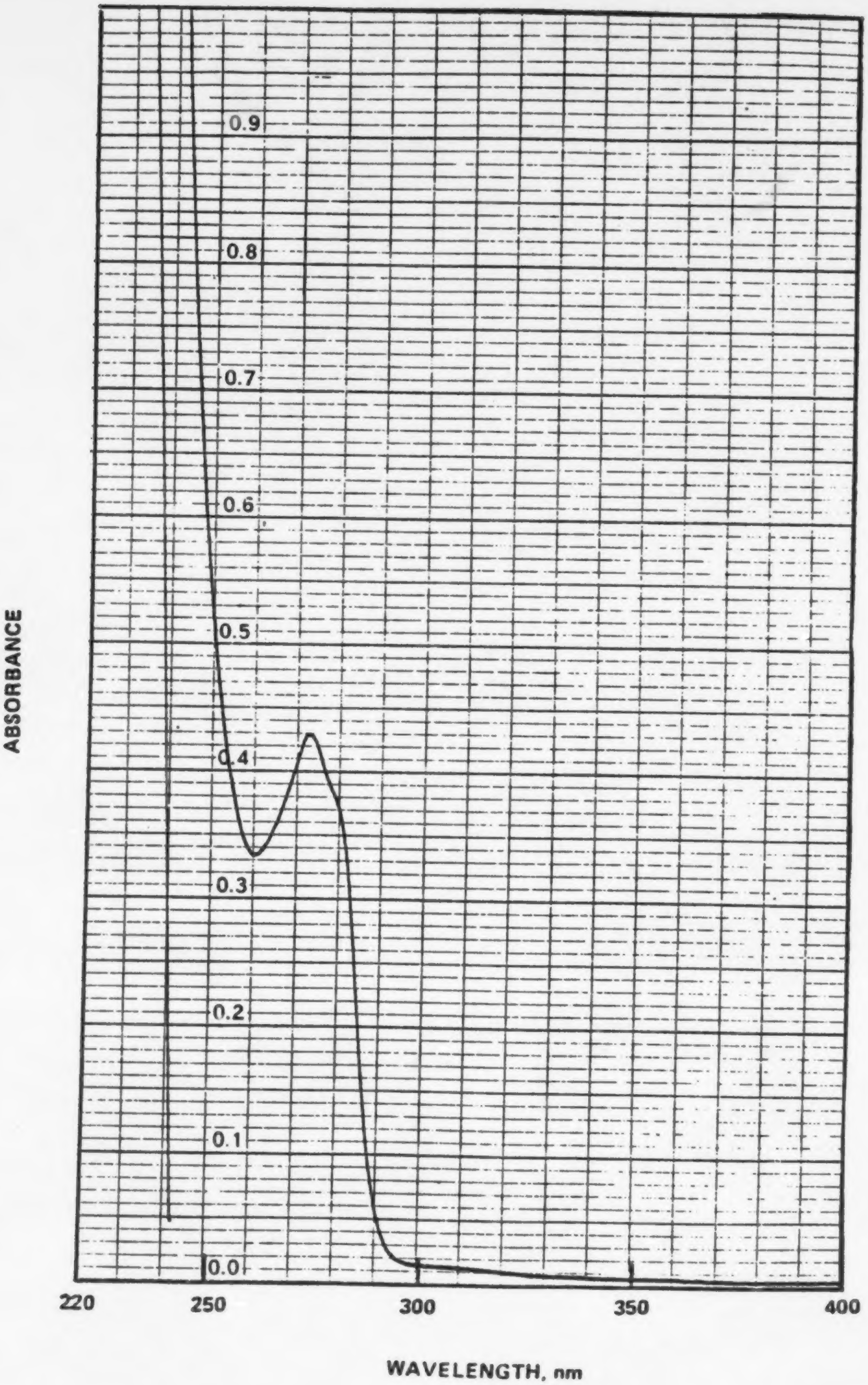


Figure C-35. UV spectrum of di-n-butyl phthalate.

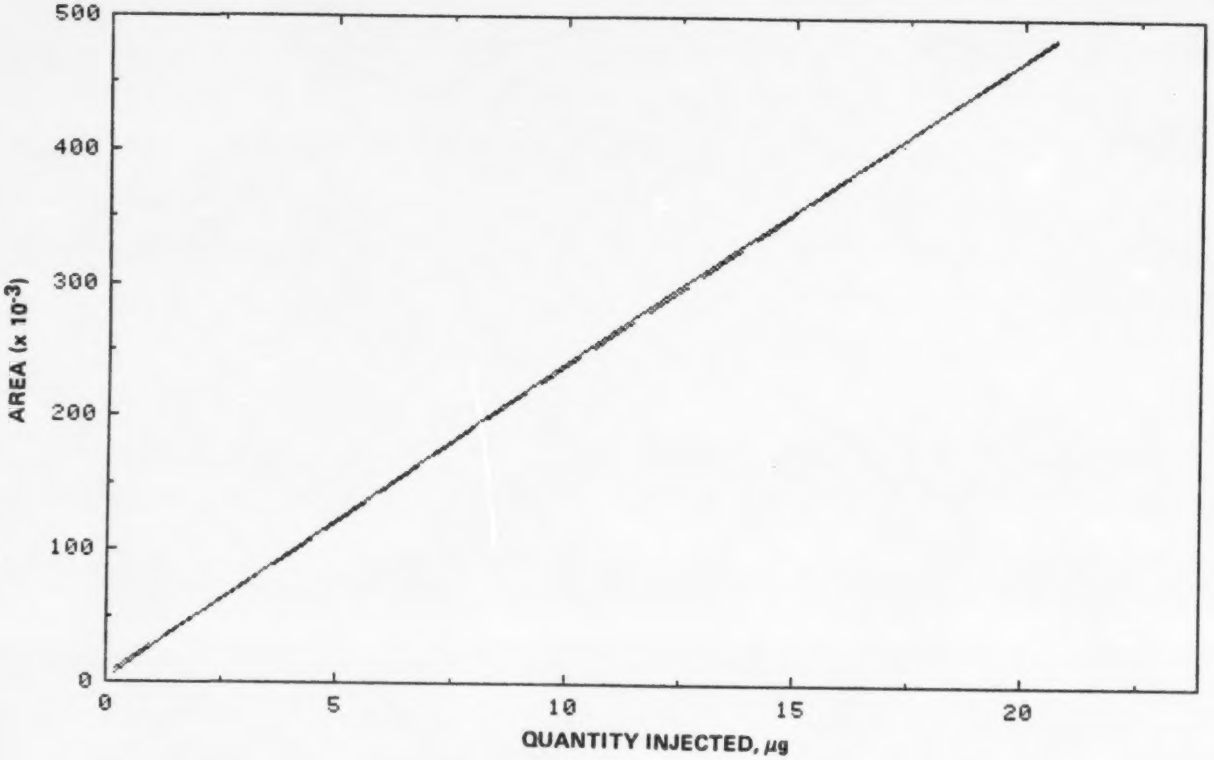


Figure C-36. Calibration curve for the determination of di-n-butyl phthalate by HPLC/UV.

Range: 0.5-20 μg
Correlation coefficient: 0.999
Slope: 2.33×10^1
y-Intercept: 4.76

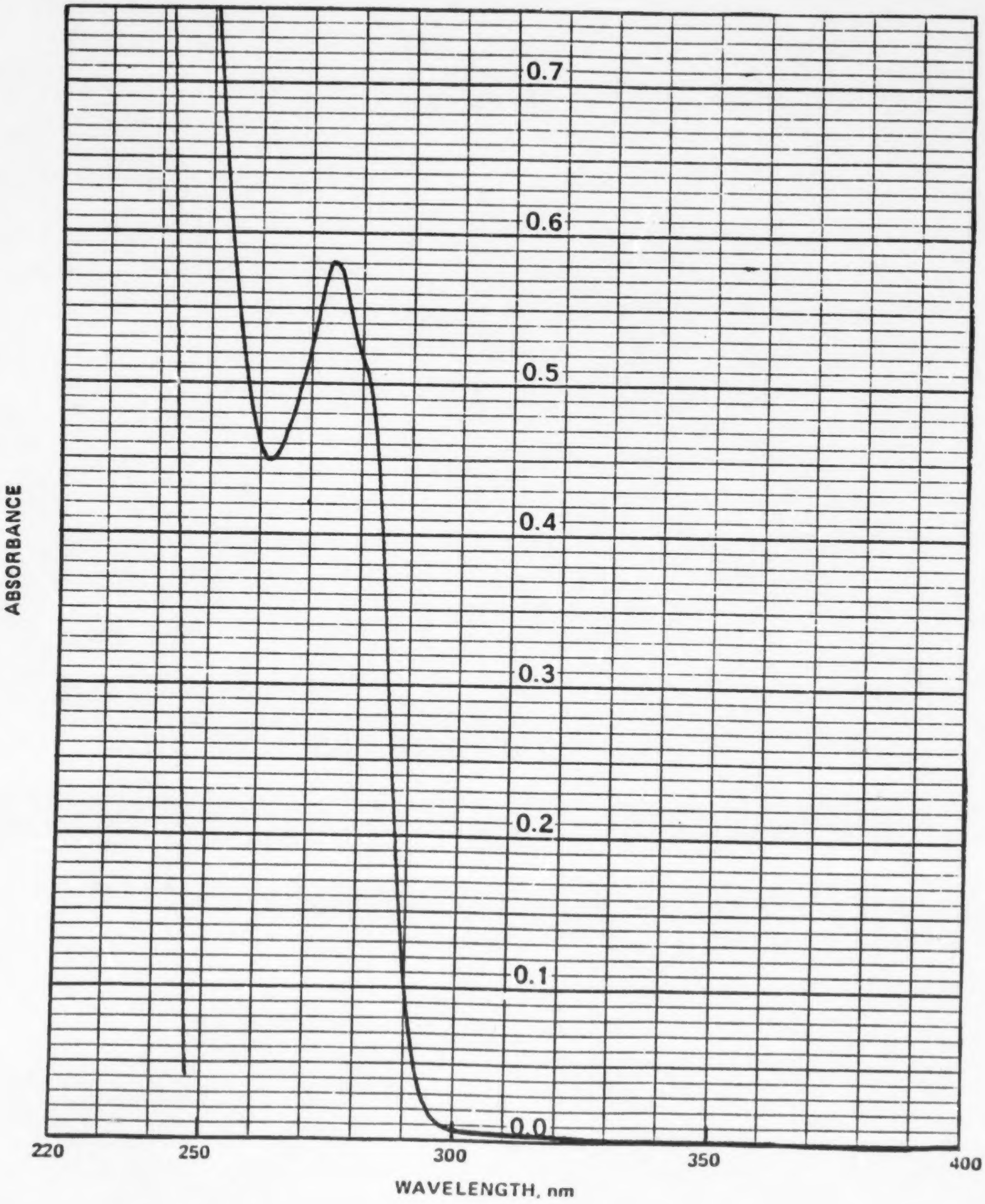


Figure C-37. UV spectrum of bis(2-ethylhexyl) phthalate.

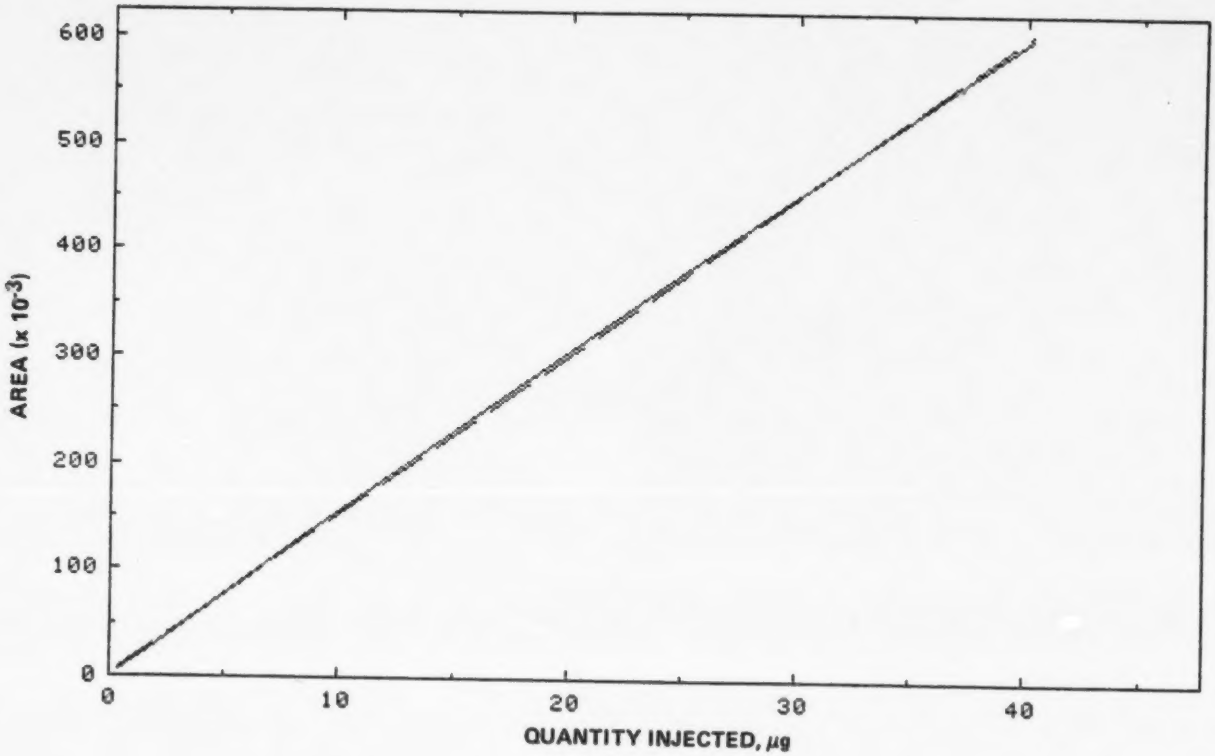


Figure C-38. Calibration curve for the determination of bis(2-ethylhexyl) phthalate by HPLC/UV.

Range: 1-40 µg
Correlation coefficient: 0.983
Slope: 1.39×10^1
y-Intercept: 3.37×10^1

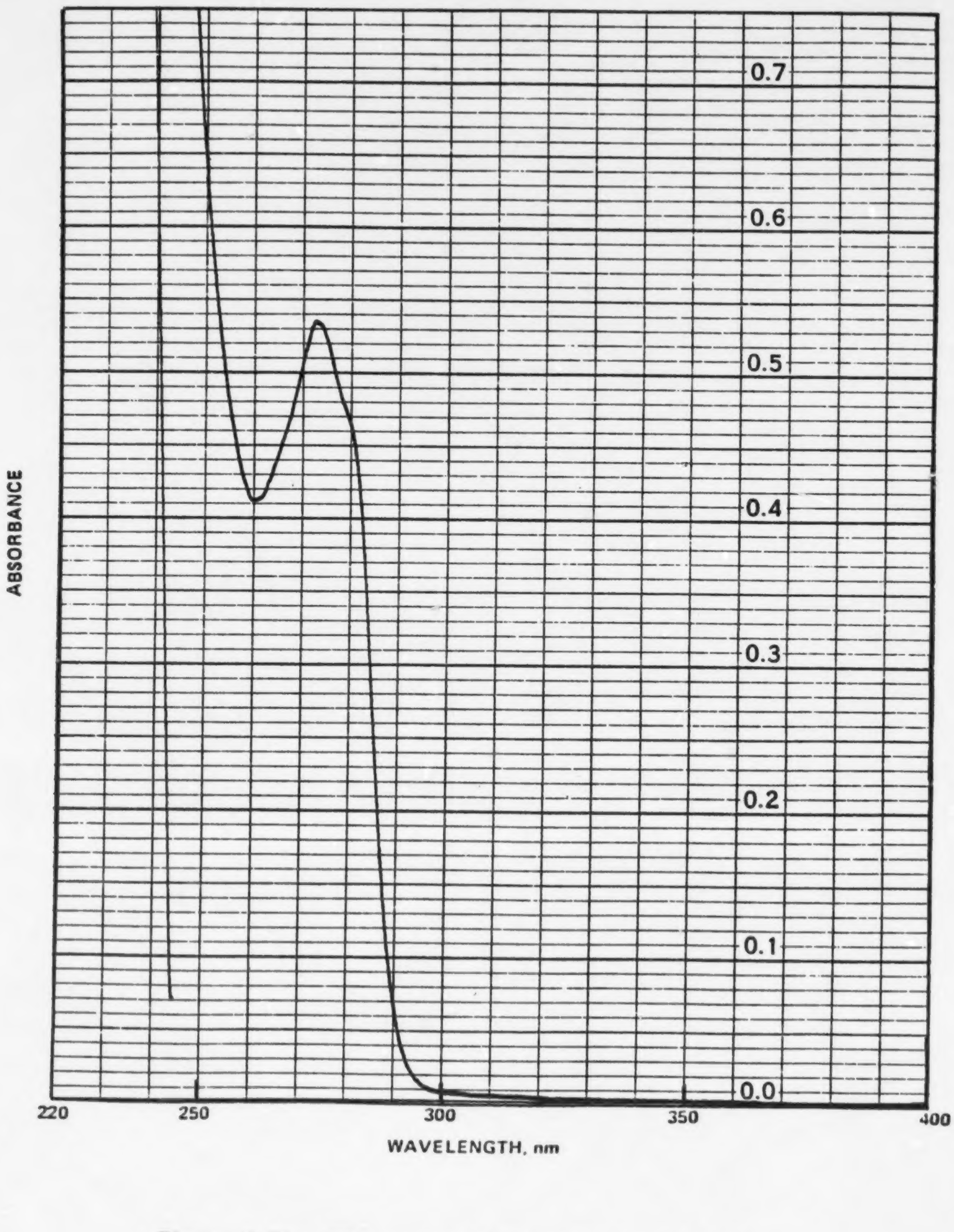


Figure C-39. UV spectrum of di-n-octyl phthalate.

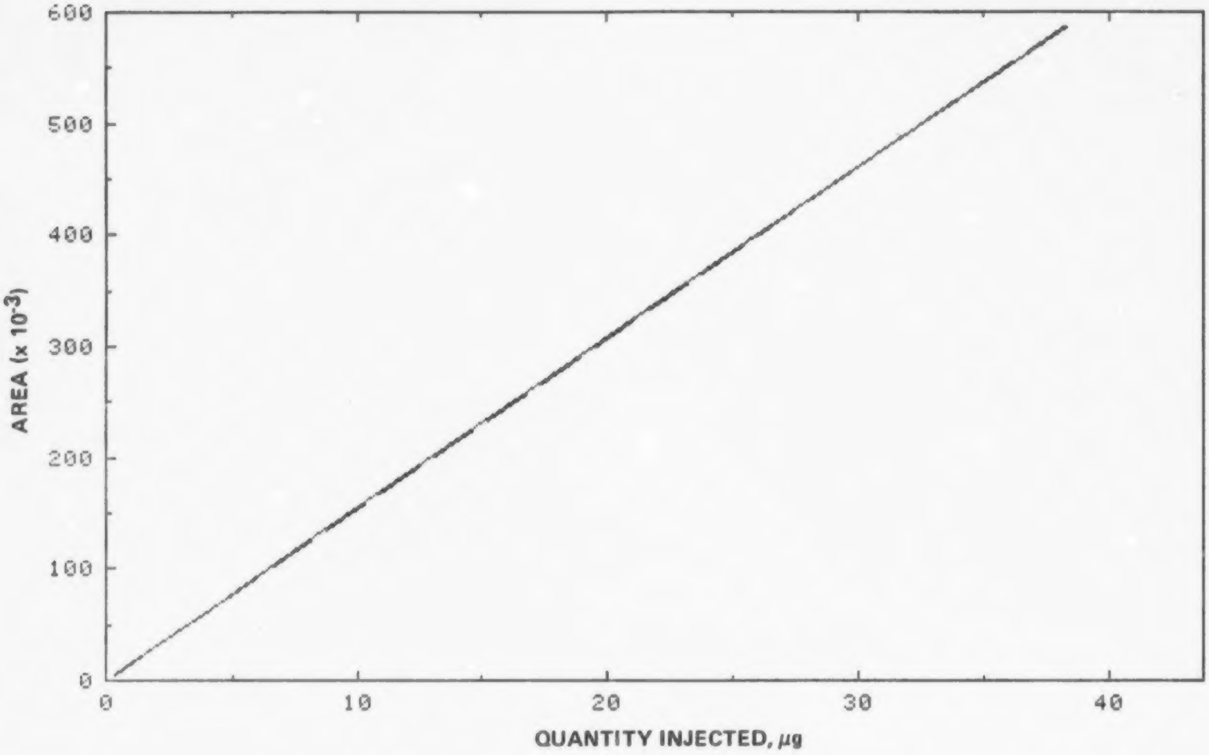


Figure C-40. Calibration curve for the determination of di-n-octyl phthalate by HPLC/UV.

Range: 0.5-40 μg
Correlation coefficient: 0.999
Slope: 1.53×10^{1}
y-Intercept: 7.91×10^{-1}

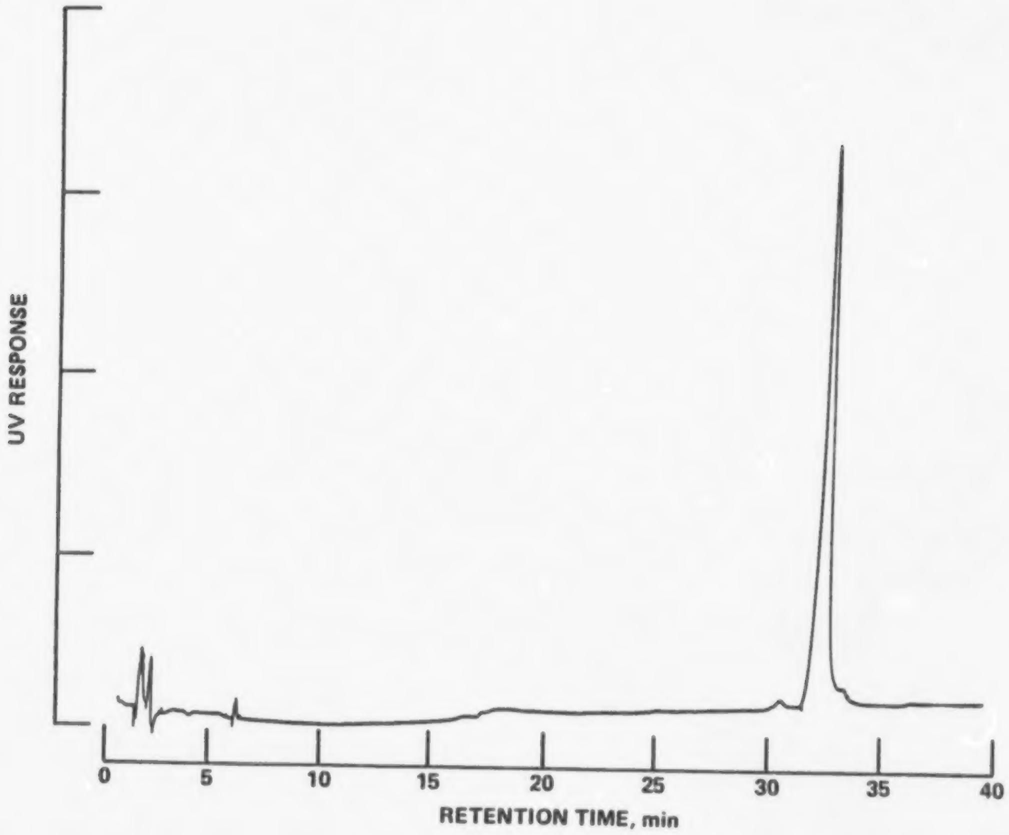


Figure C-41. Chromatogram by HPLC/UV for chrysene.

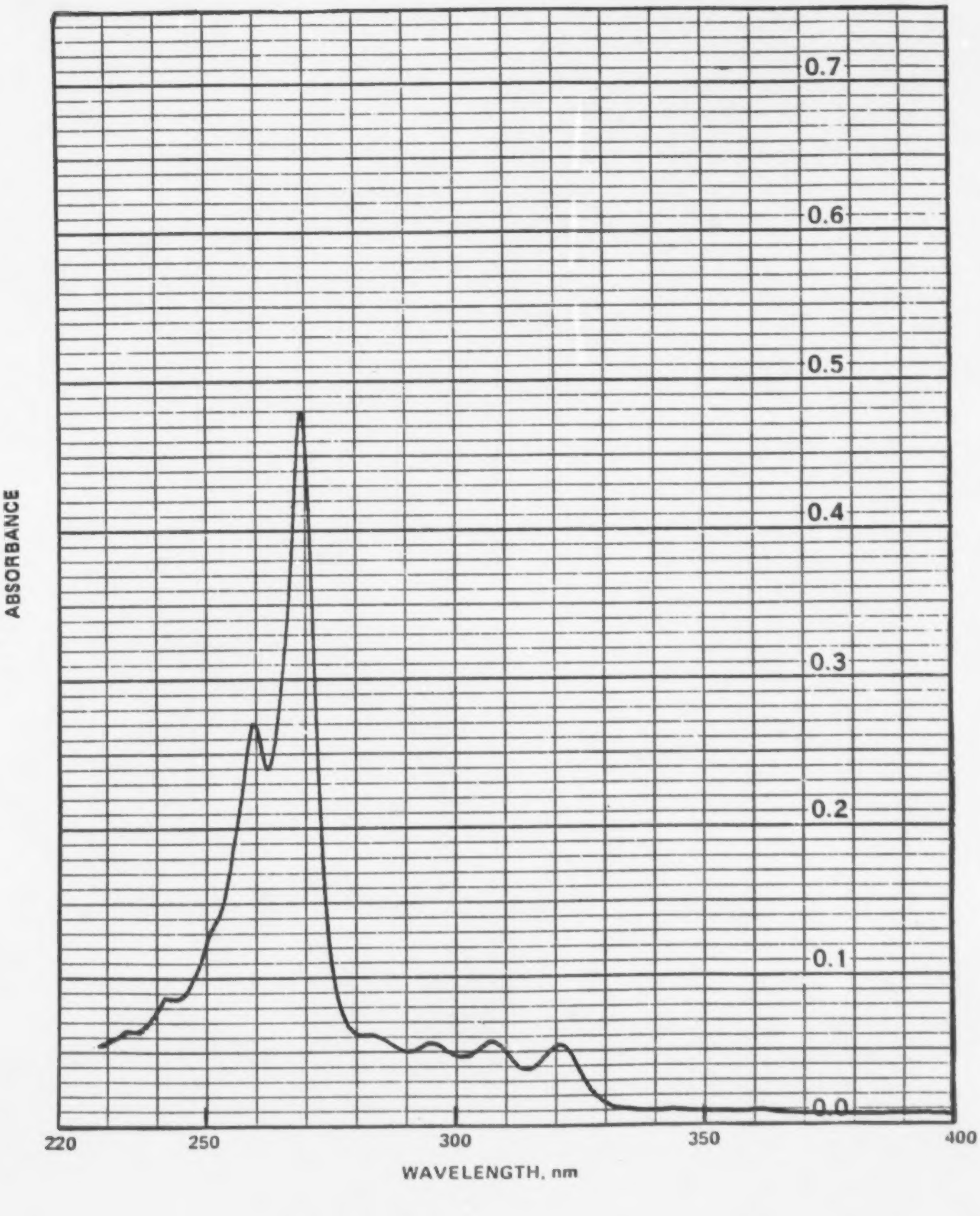


Figure C-42. UV spectrum of chrysene.

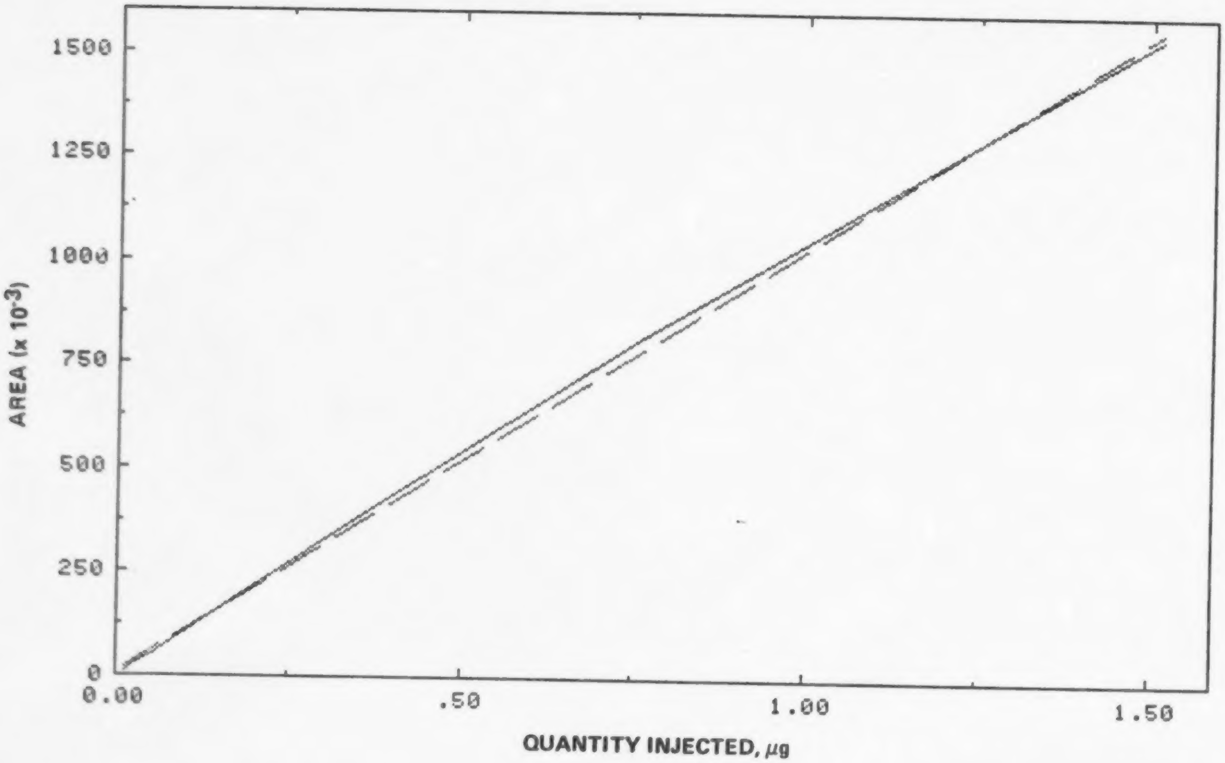


Figure C-43. Calibration curve for the determination of chrysene by HPLC/UV.

Range: 0.02-1.5 μg
Correlation coefficient: 0.999
Slope: 1.03 x 10^3
y-Intercept: 6.64

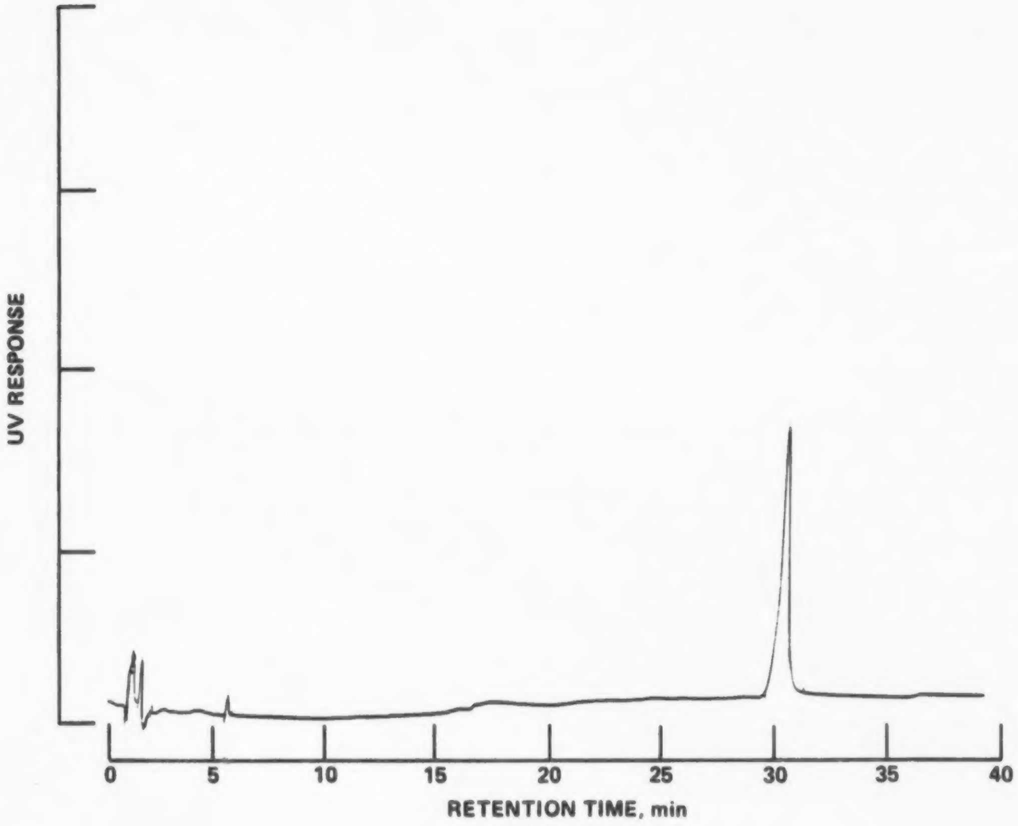


Figure C-44. Chromatogram by HPLC/UV for dibenz(a,j)acridine.

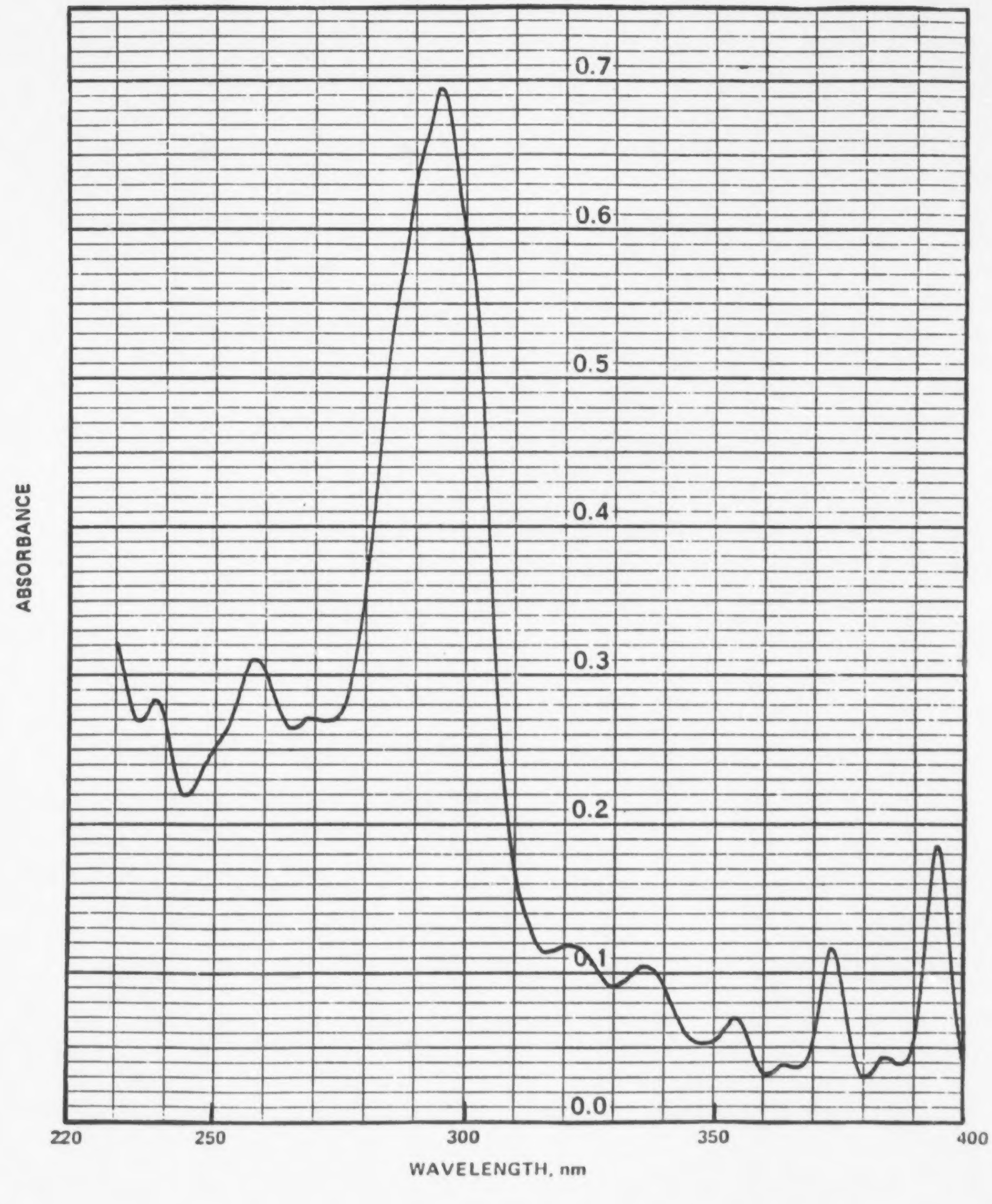


Figure C-45. UV spectrum of dibenz(a,j)acridine.

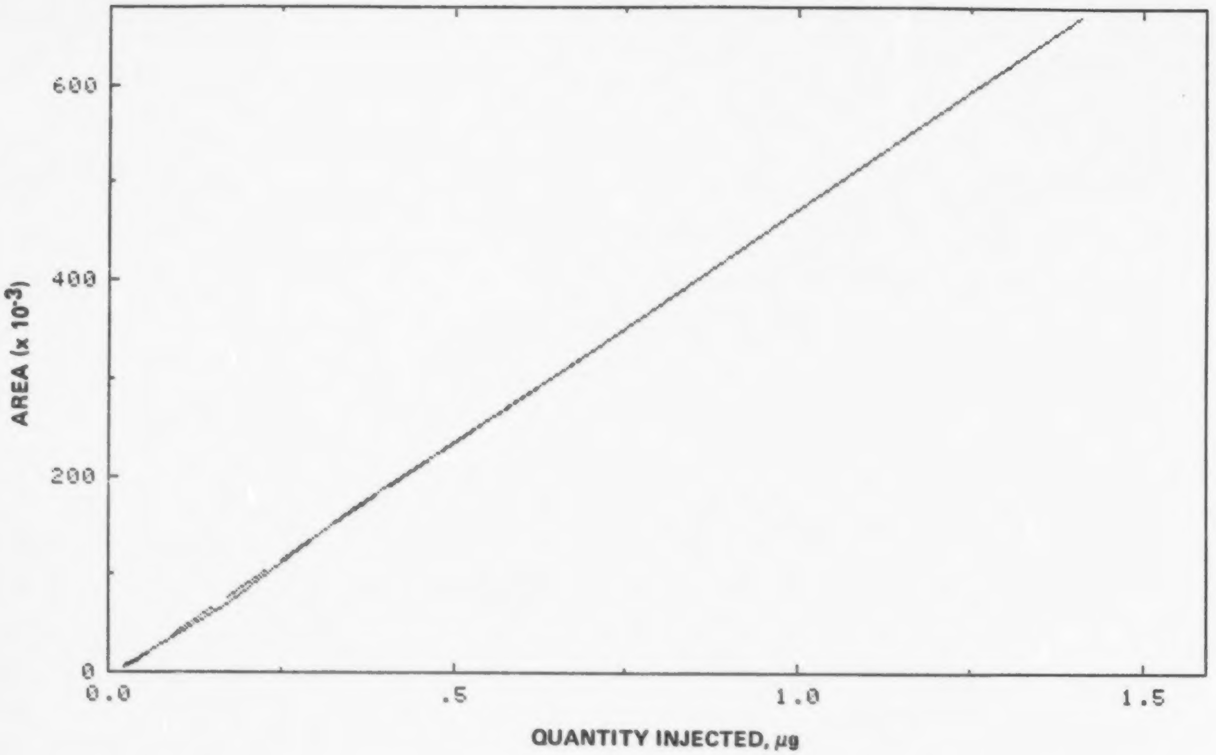


Figure C-46. Calibration curve for the determination of dibenz(a,j)acridine by HPLC/UV.

Range: 0.02-1.4 µg
Correlation coefficient: 0.999
Slope: 4.80×10^2
y-Intercept: -7.15

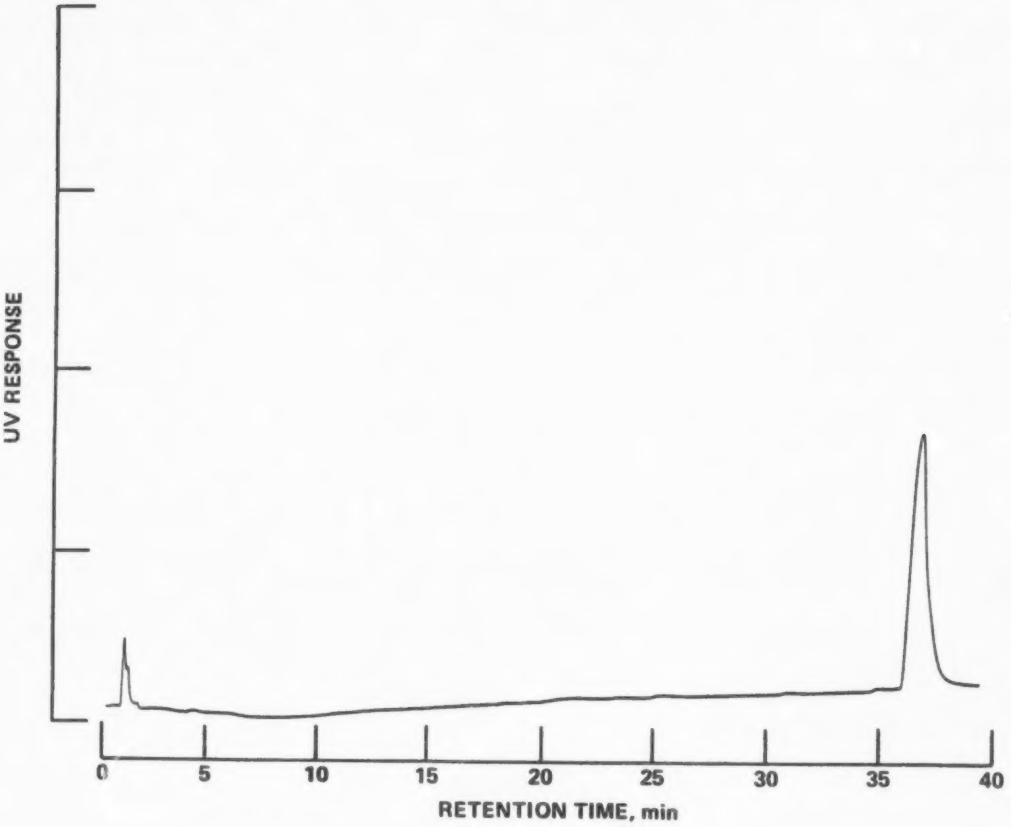


Figure C-47. Chromatogram by HPLC/UV for dibenz(a,h)anthracene.

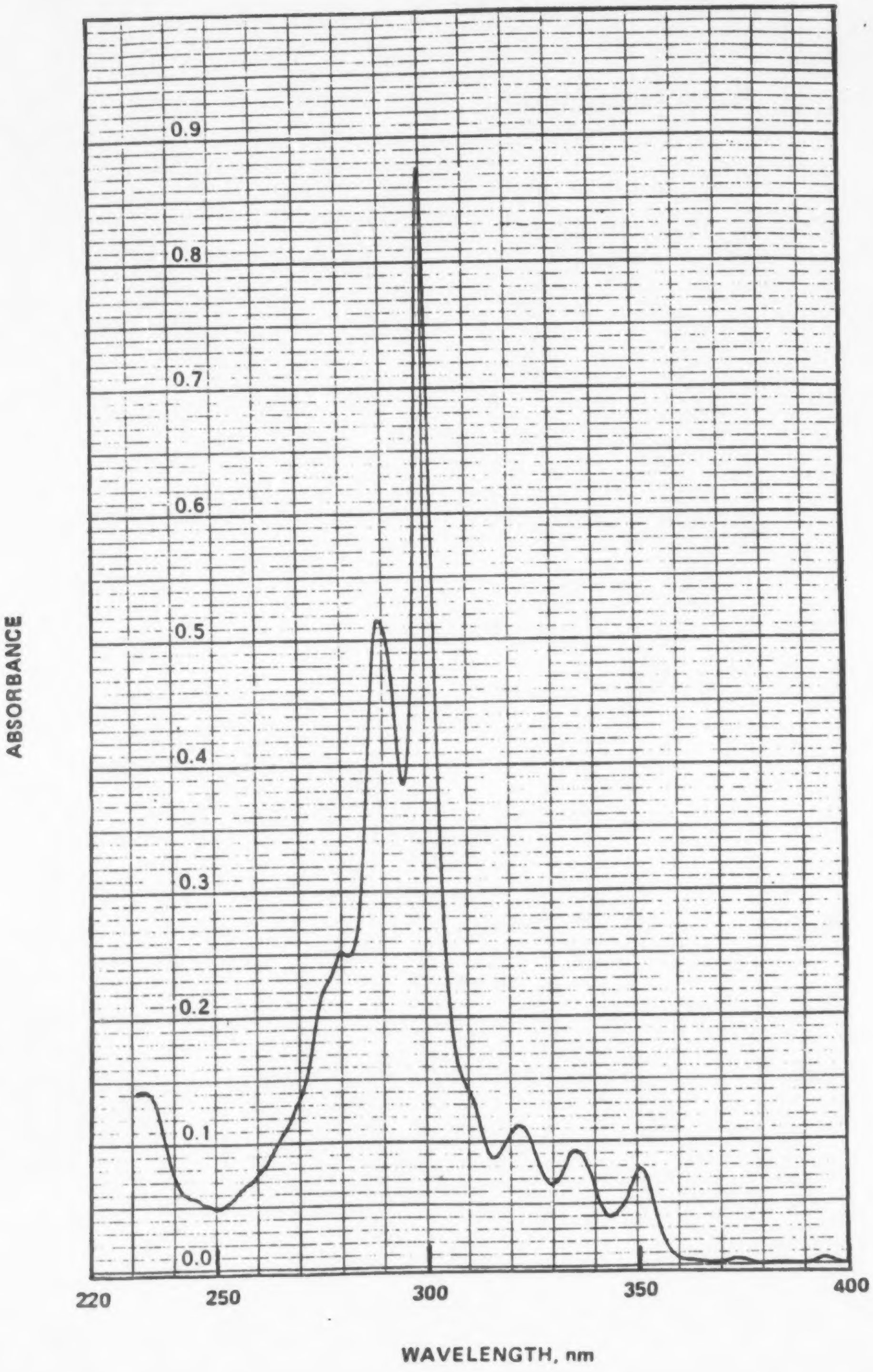


Figure C-48. UV spectrum of dibenz(a,h)anthracene.

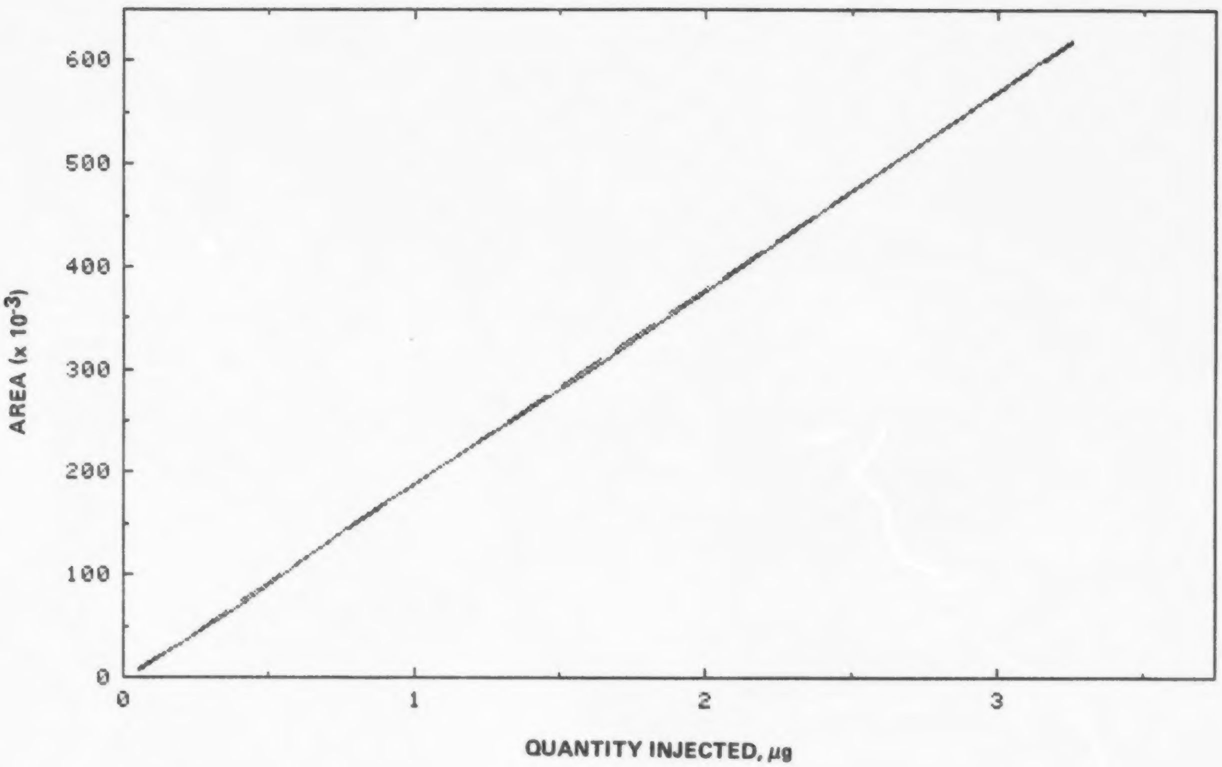


Figure C-49. Calibration curve for the determination of dibenz(a,h)anthracene by HPLC/UV.

Range: 0.05-3.0 μg
Correlation coefficient: 0.999
Slope: 1.91×10^2
y-Intercept: -4.03

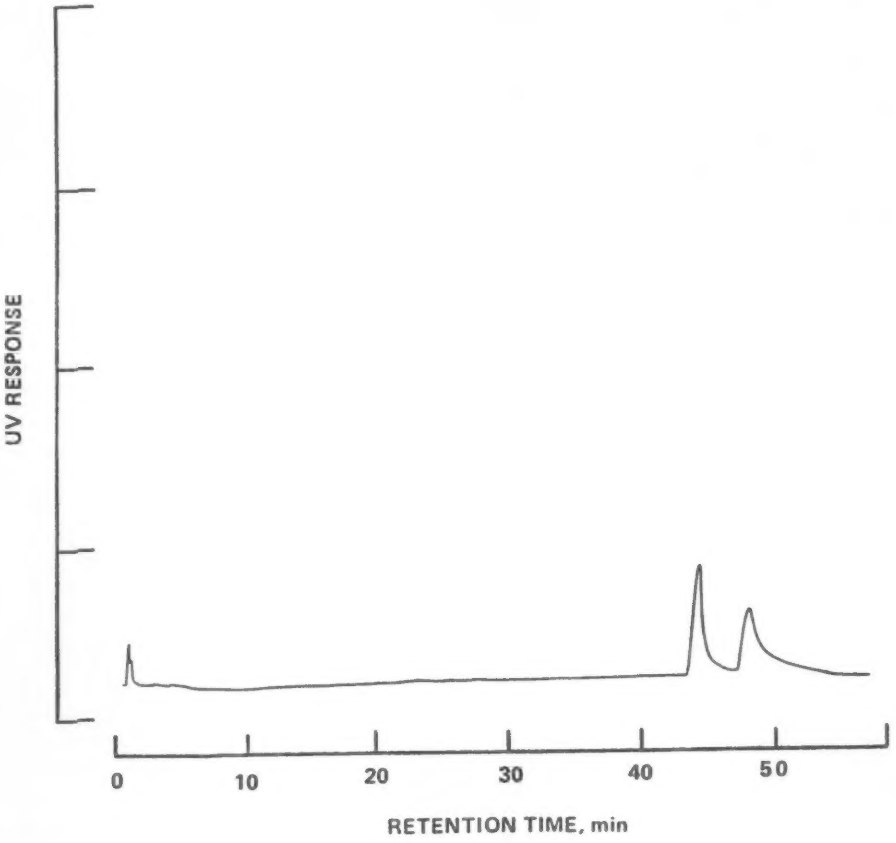


Figure C-50. Chromatogram by HPLC/UV for dibenzo(a,i)pyrene (t_R = 48.4 min).

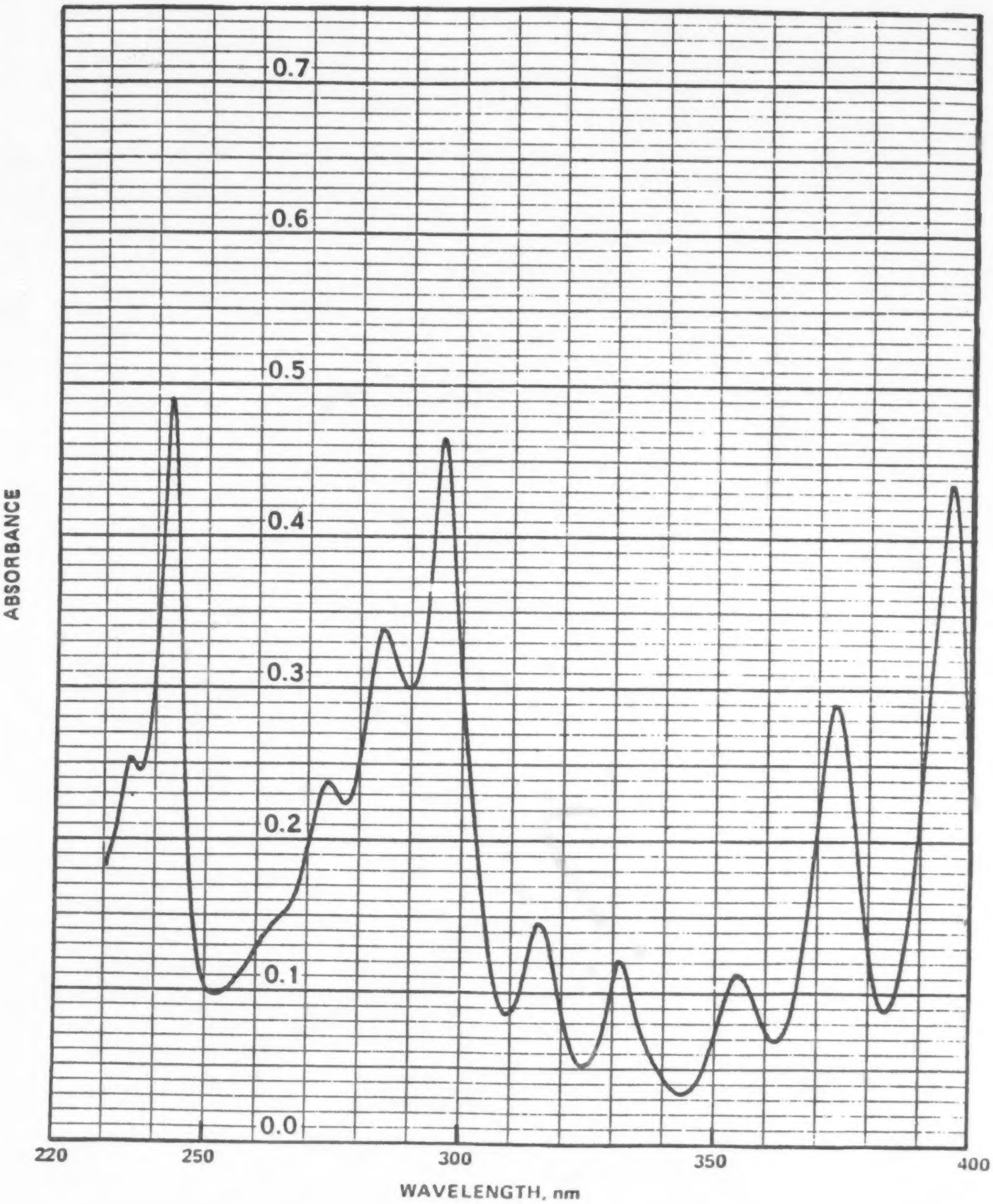


Figure C-51. UV spectrum of dibenzo(a,i)pyrene.

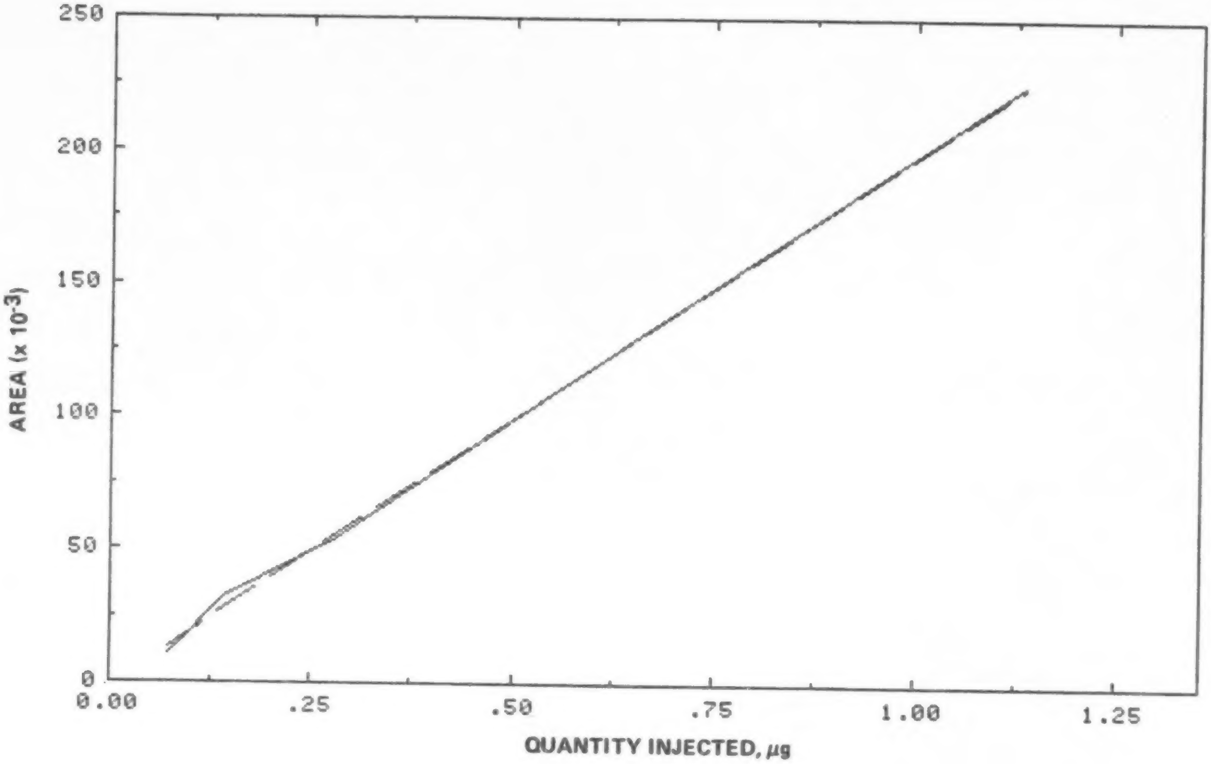


Figure C-52. Calibration curve for the determination of dibenzo(a,i)pyrene by HPLC/UV.

Range: 0.05-1.0 µg
Correlation coefficient: 0.999
Slope: 1.99×10^2
y-Intercept: -6.26×10^{-1}

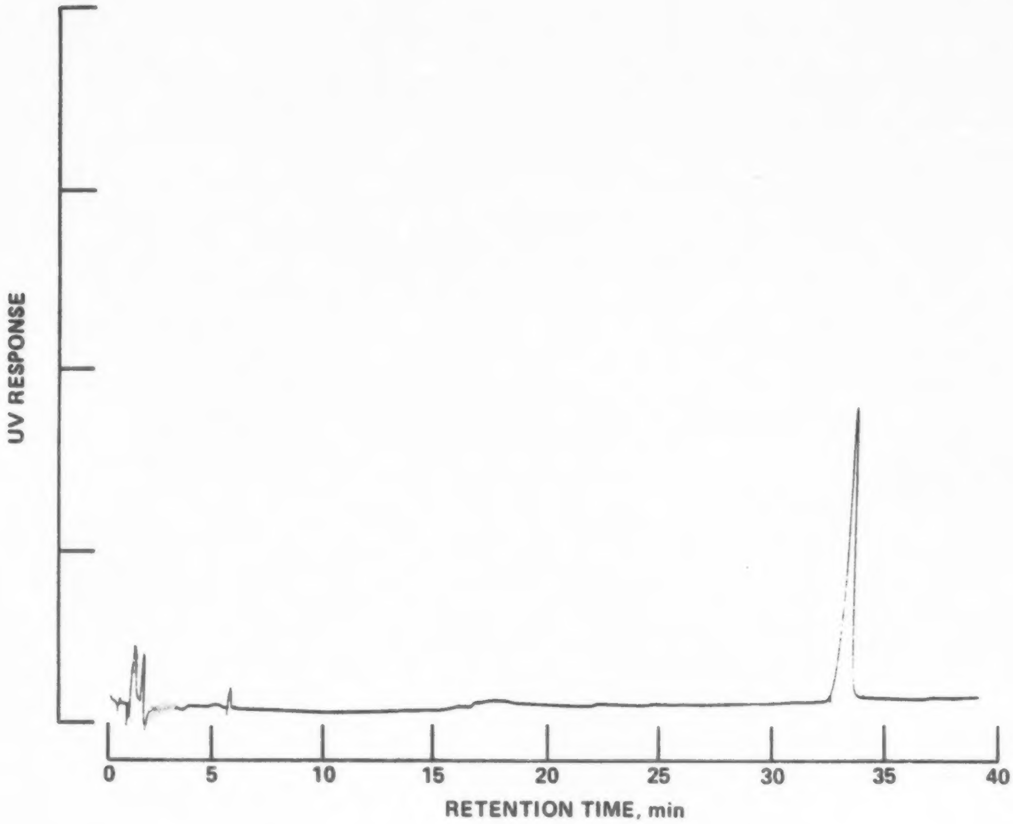


Figure C-53. Chromatogram by HPLC/UV for 7,12-dimethylbenz(a)anthracene.

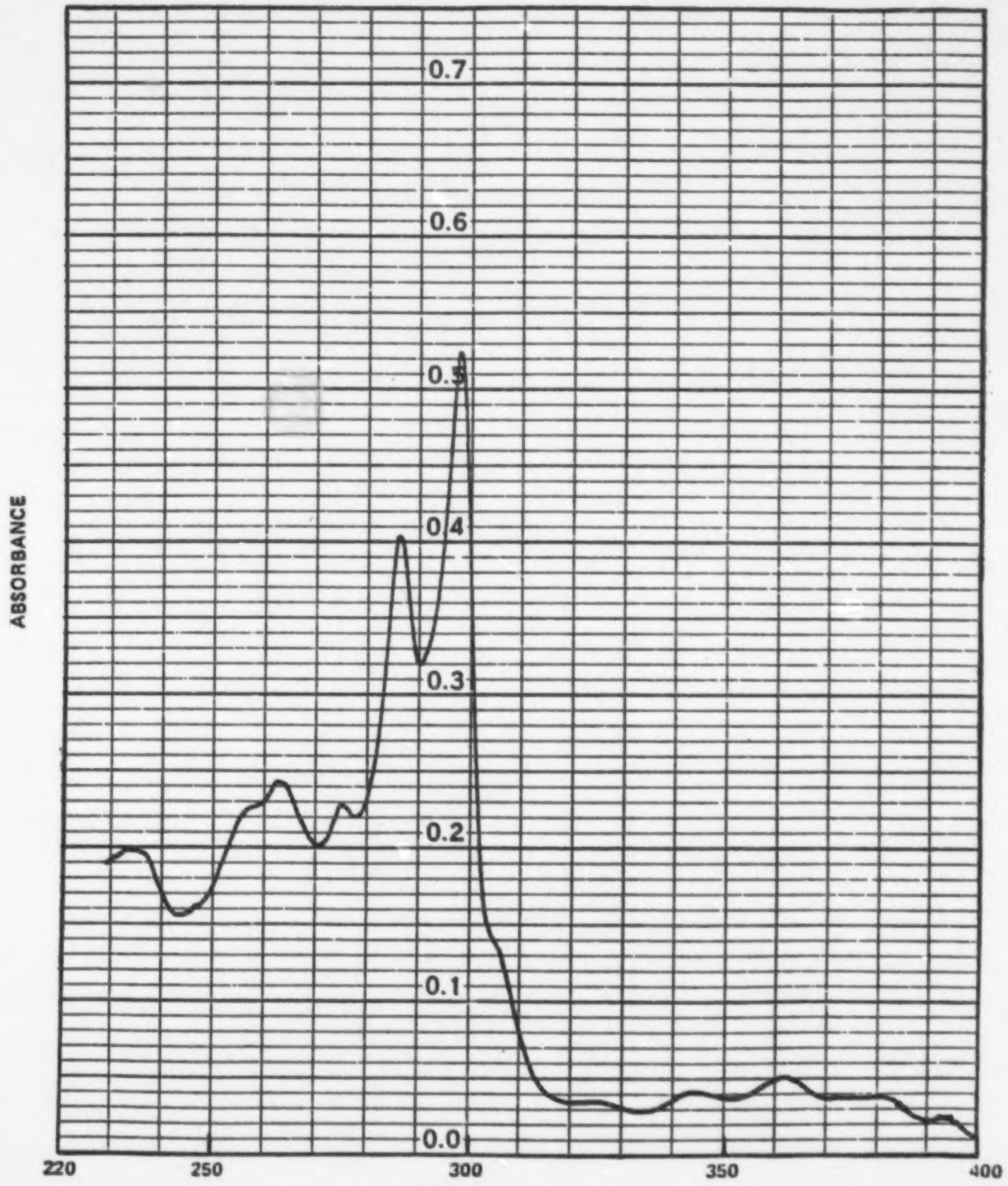


Figure C-54. UV spectrum of 7,12-dimethylbenz(a)anthracene.

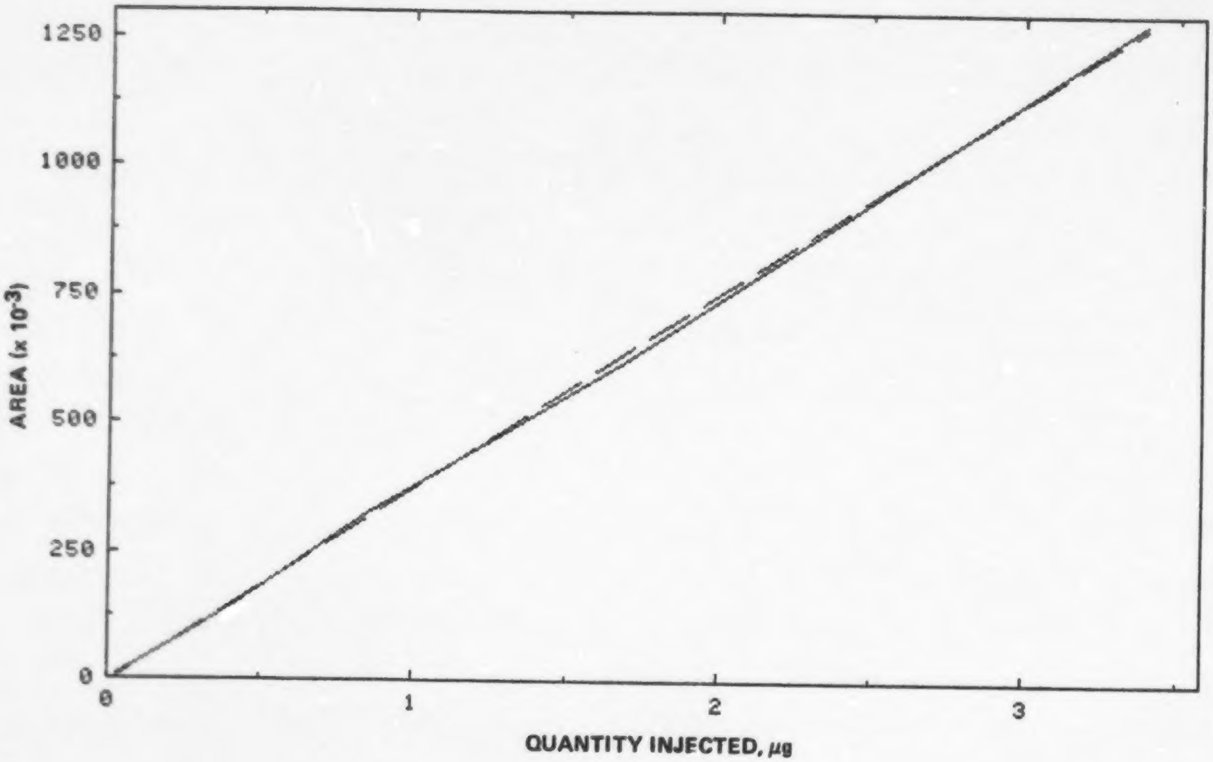


Figure C-55. Calibration curve for the determination of 7,12-dimethylbenz(a)anthracene by HPLC/UV.

Range: 0.02-3 µg
Correlation coefficient: 0.999
Slope: 3.78×10^2
y-Intercept: -5.44

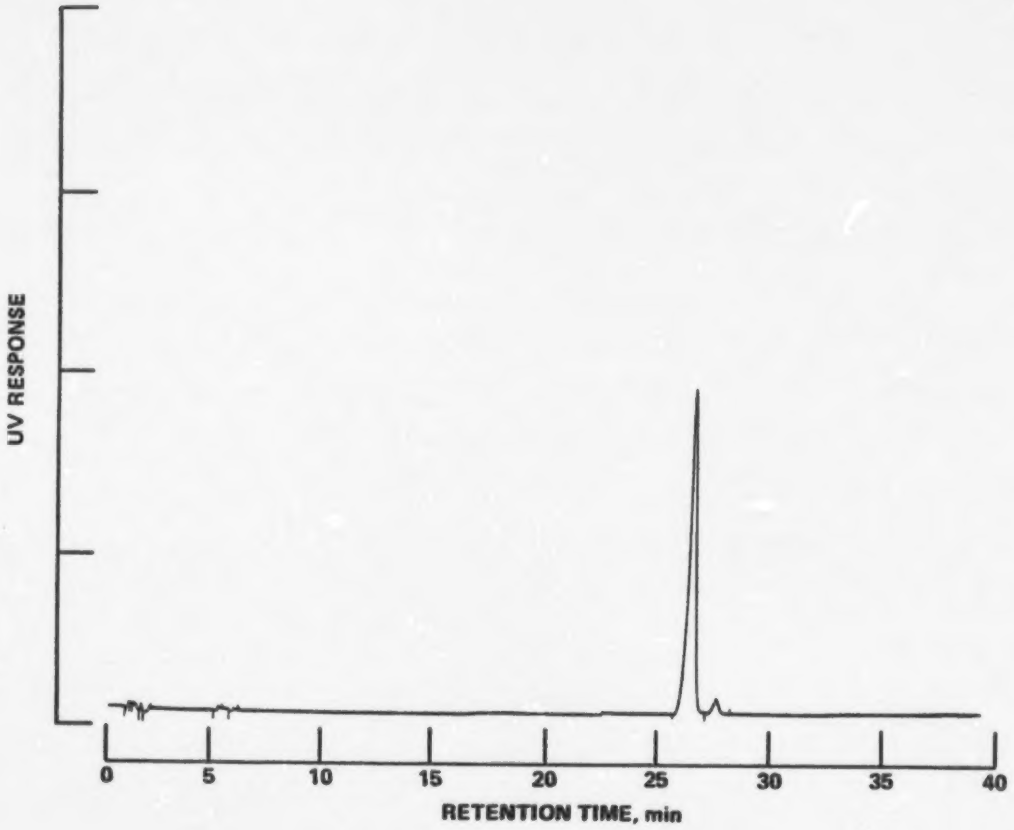


Figure C-56. Chromatogram by HPLC/UV for fluoranthene.

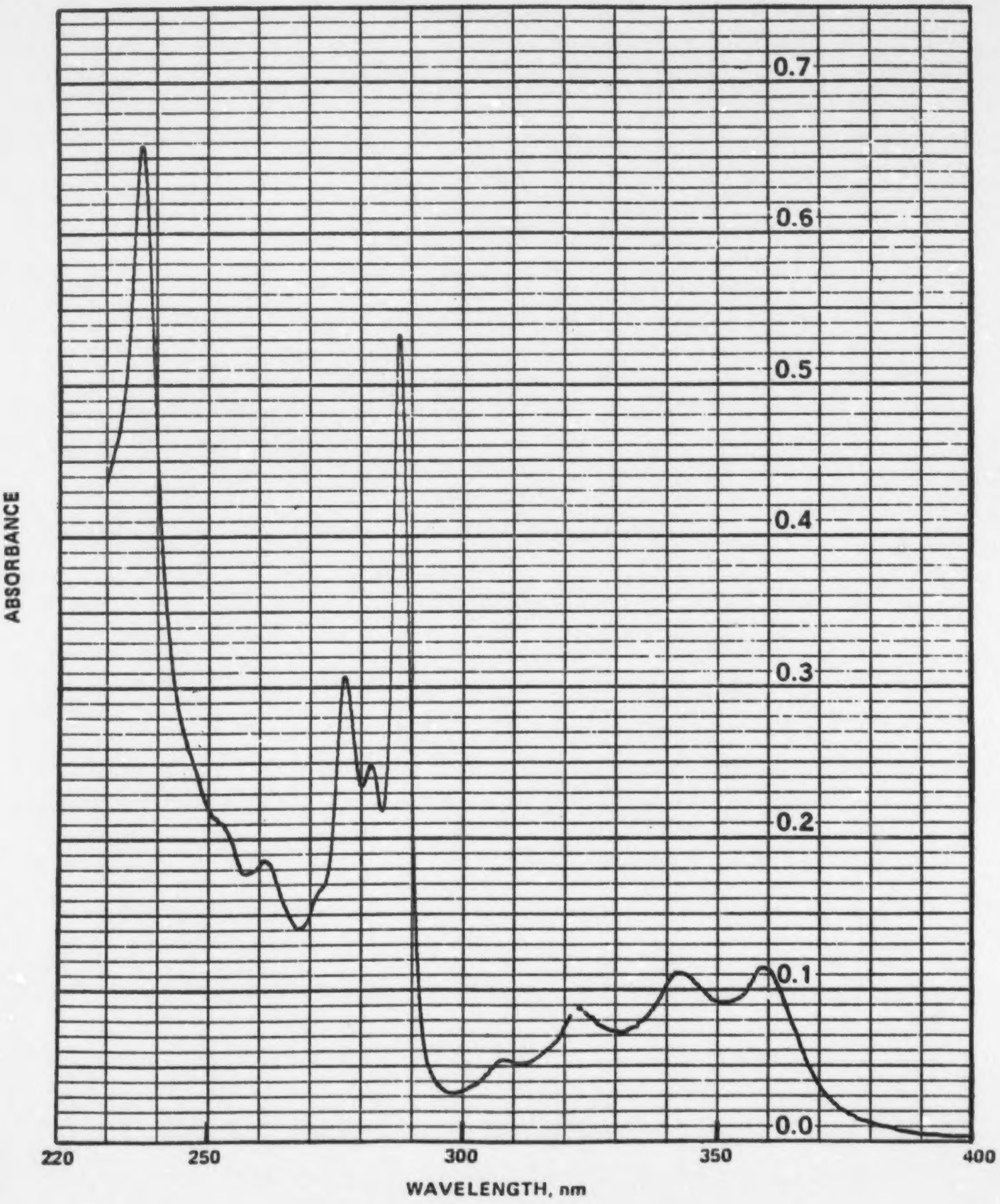


Figure C-57. UV spectrum of fluoranthene.

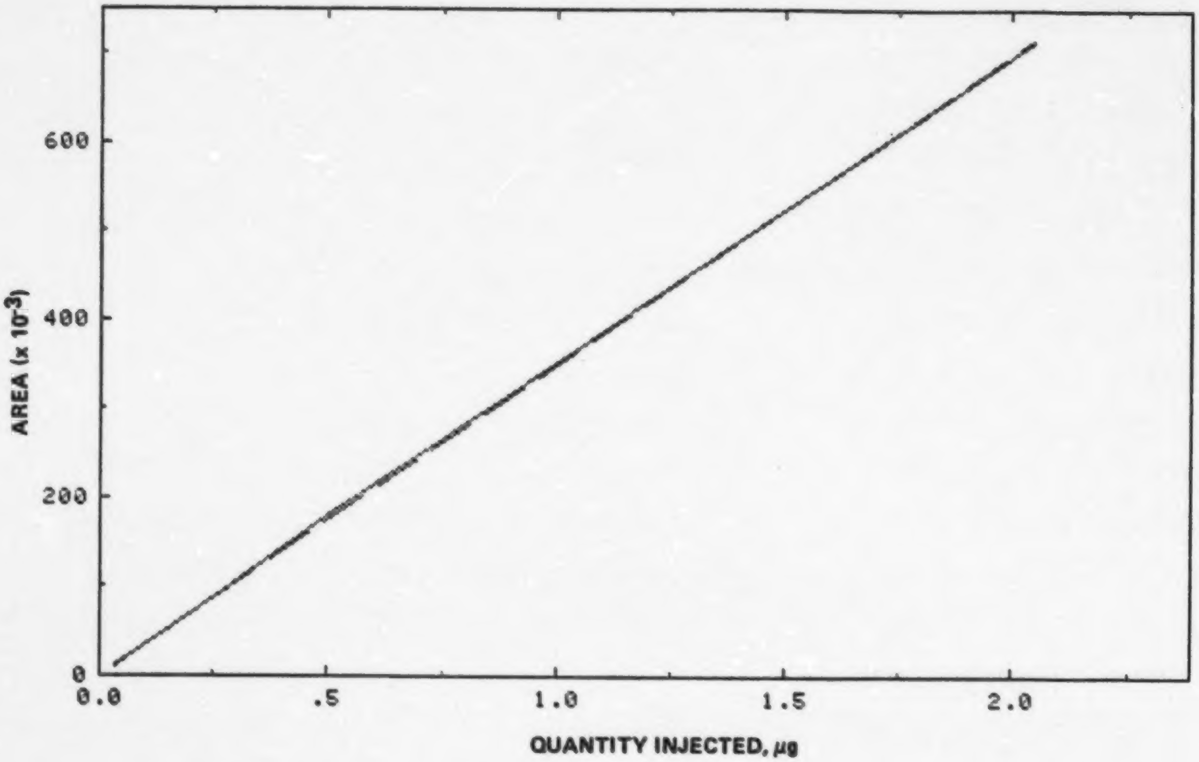


Figure C-58. Calibration curve for the determination of fluoranthene by HPLC/UV.

Range: 0.005-2 µg
Correlation coefficient: 0.999
Slope: 3.49×10^2
y-Intercept: 4.48×10^{-1}

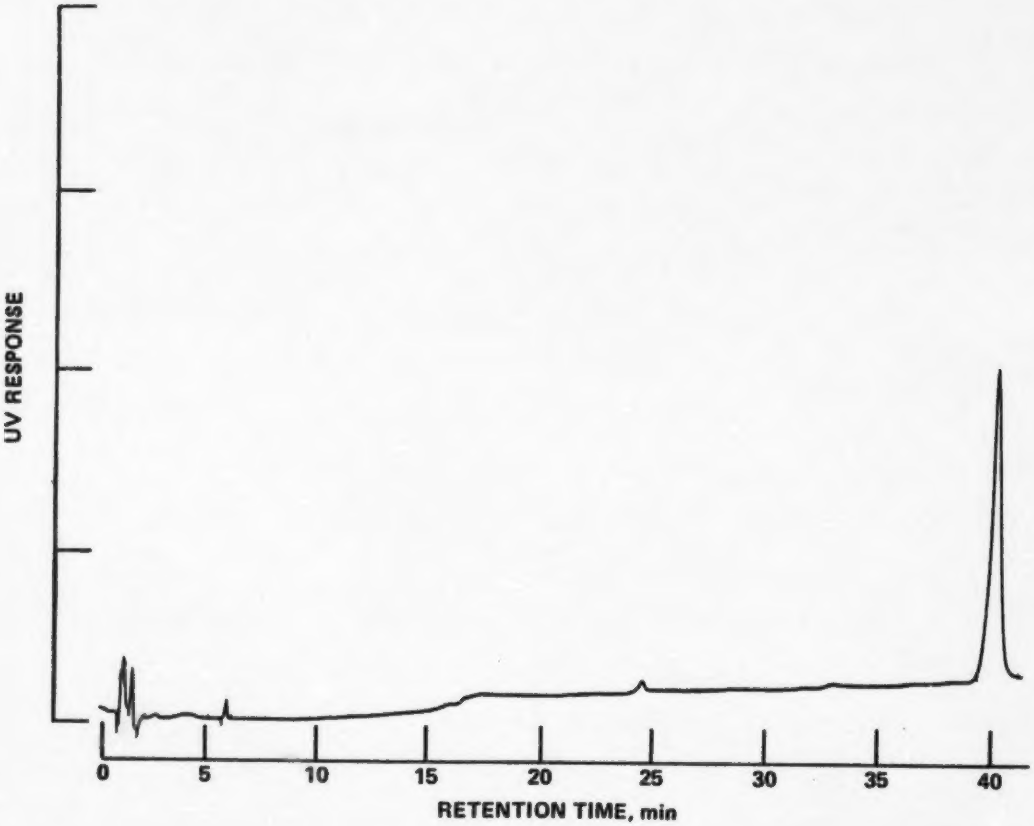


Figure C-59. Chromatogram by HPLC/UV for indeno(1,2,3-c,d)pyrene.

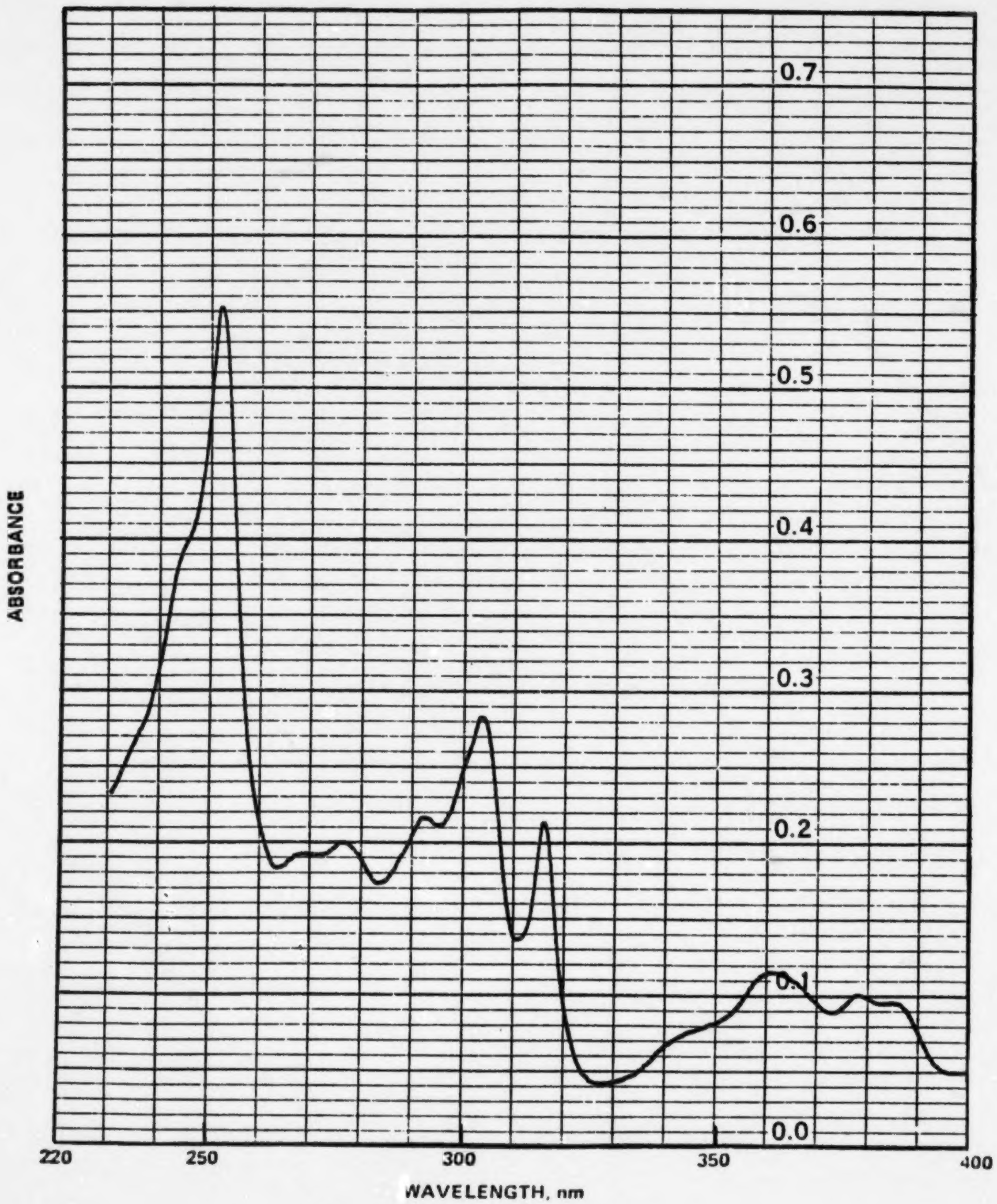


Figure C-60. UV spectrum of indeno(1,2,3-c,d)pyrene.

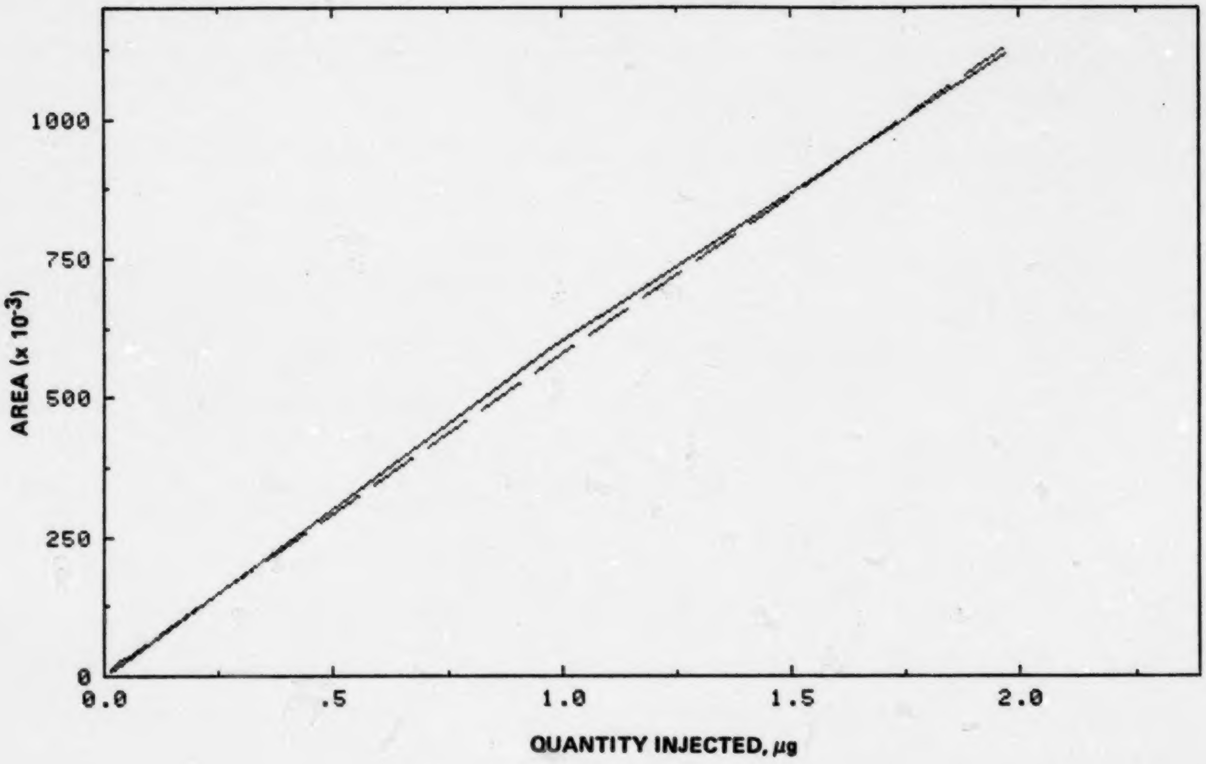


Figure C-61. Calibration curve for the determination of indeno(1,2,3-c,d)pyrene by HPLC/UV.

Range: 0.02-2 μg
Correlation coefficient: 0.999
Slope: 5.72×10^2
y-Intercept: 4.95

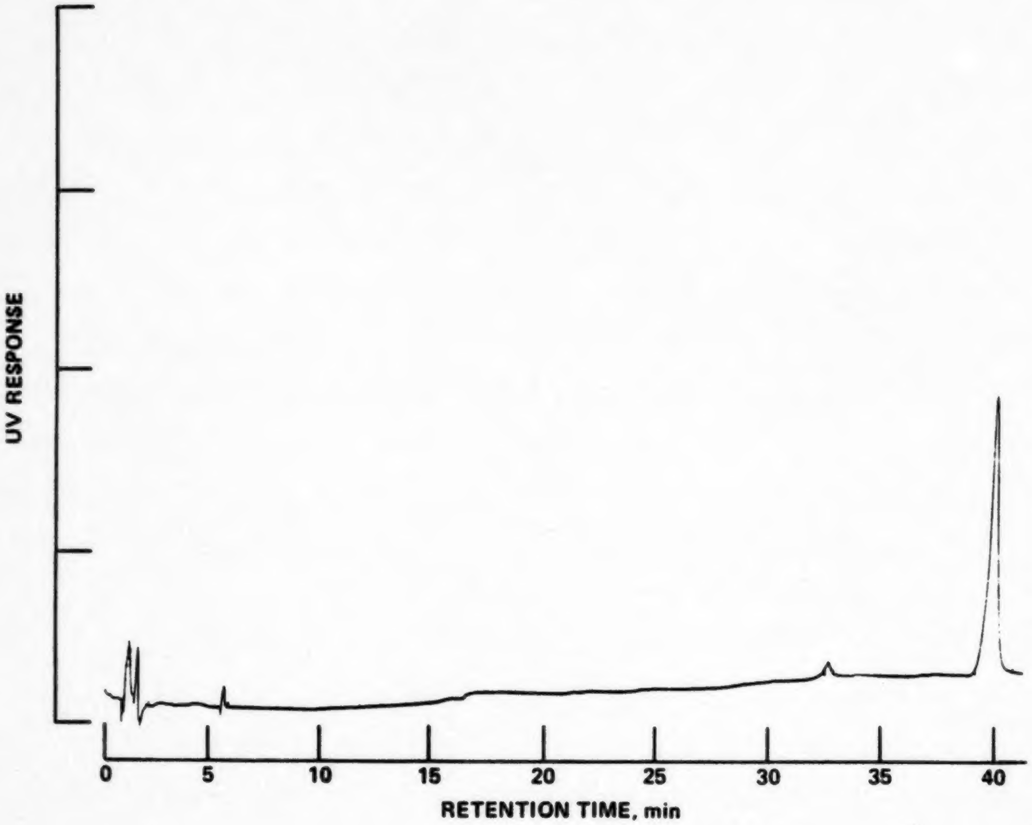


Figure C-62. Chromatogram by HPLC/UV for 3-methylcholanthrene.

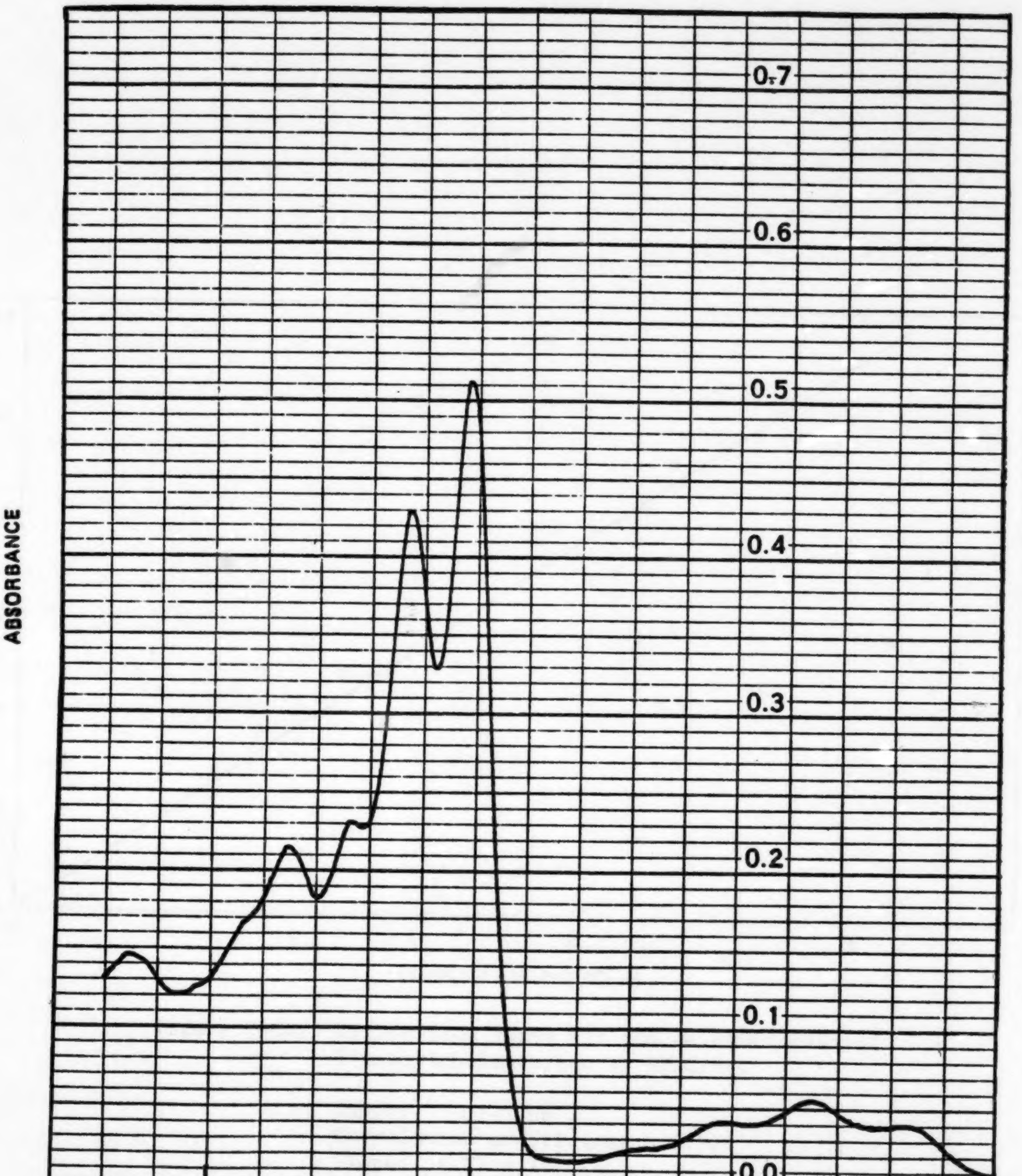


Figure C-63. UV spectrum of 3-methylcholanthrene.

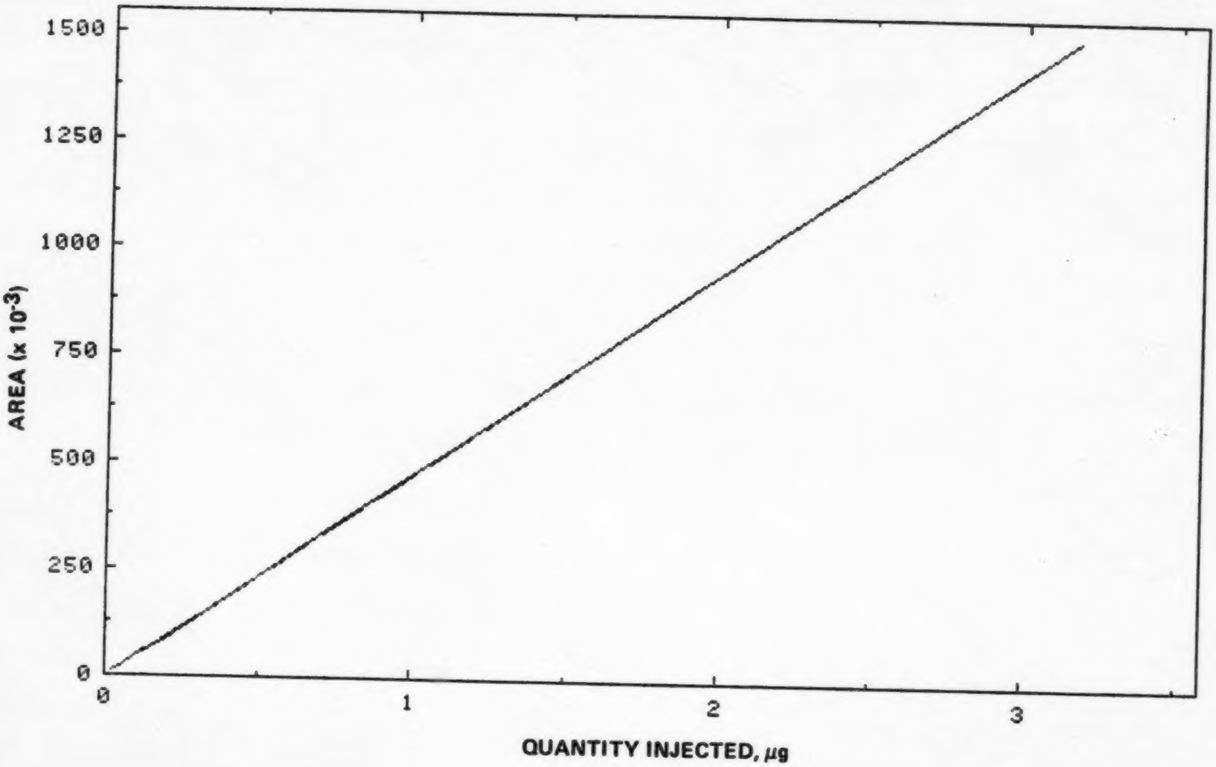


Figure C-64. Calibration curve for the determination of 3-methylcholanthrene by HPLC/UV.

Range: 0.01-3 μg
Correlation coefficient: 0.999
Slope: 4.77×10^2
y-Intercept: -3.12

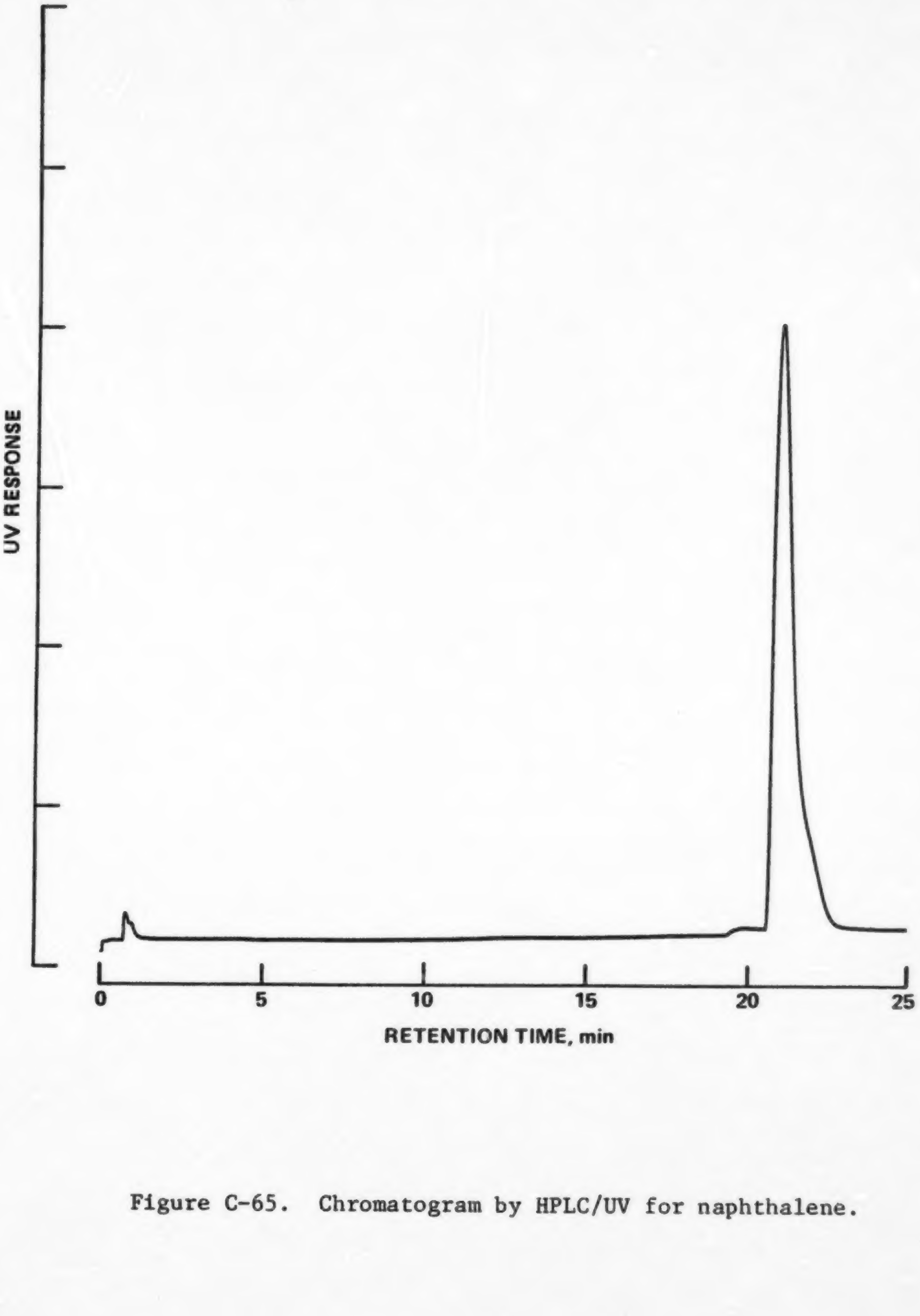


Figure C-65. Chromatogram by HPLC/UV for naphthalene.

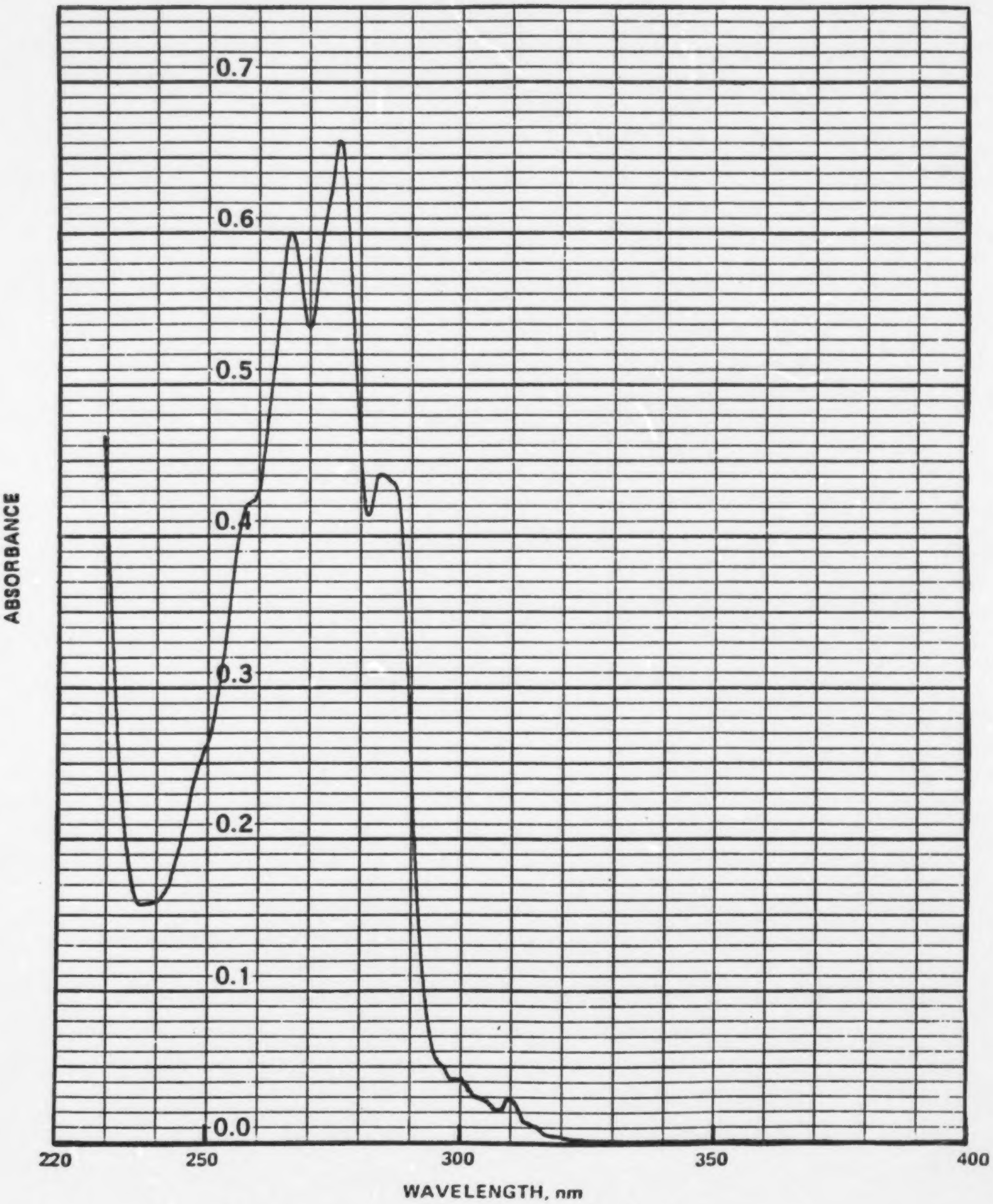


Figure C-66. UV spectrum of naphthalene.

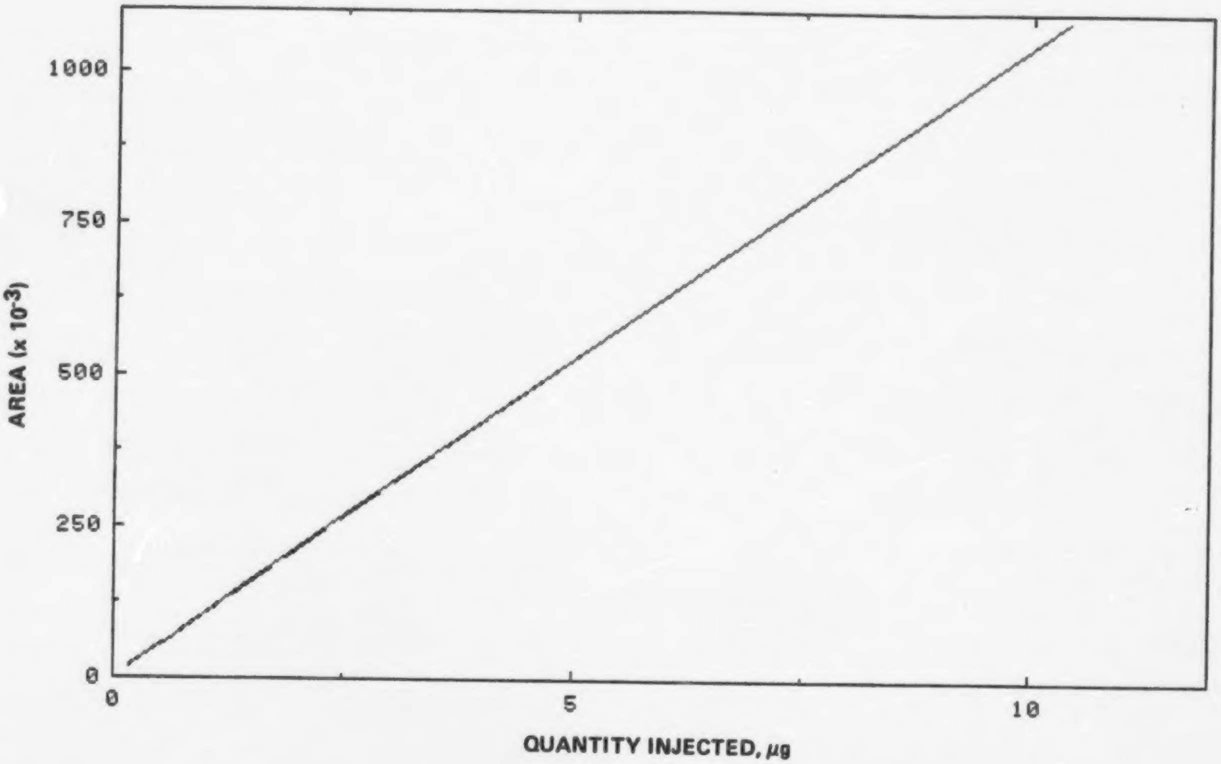


Figure C-67. Calibration curve for the determination of naphthalene by HPLC/UV.

Range: 0.05-10 µg
Correlation coefficient: 0.999
Slope: 1.04×10^2
y-Intercept: 3.50

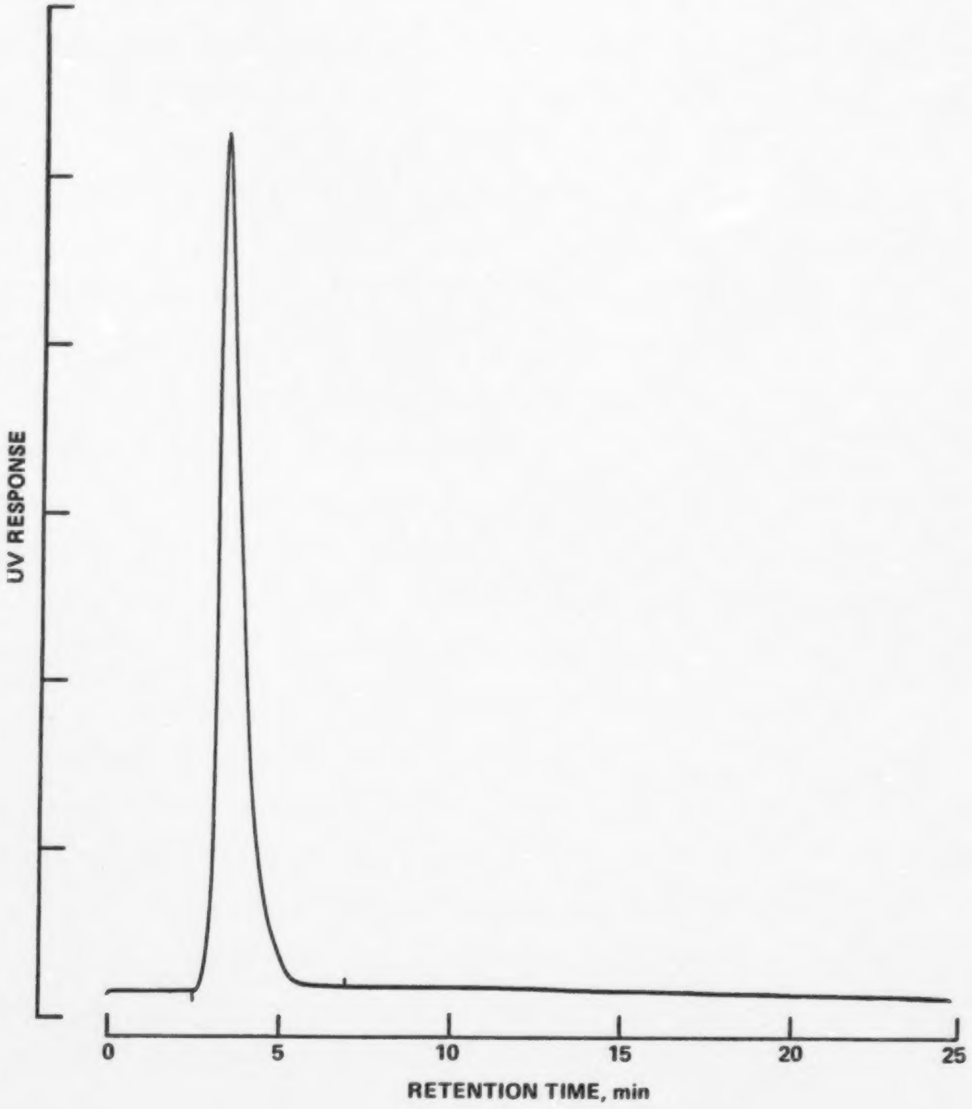


Figure C-68. Chromatogram by HPLC/UV for selenourea.

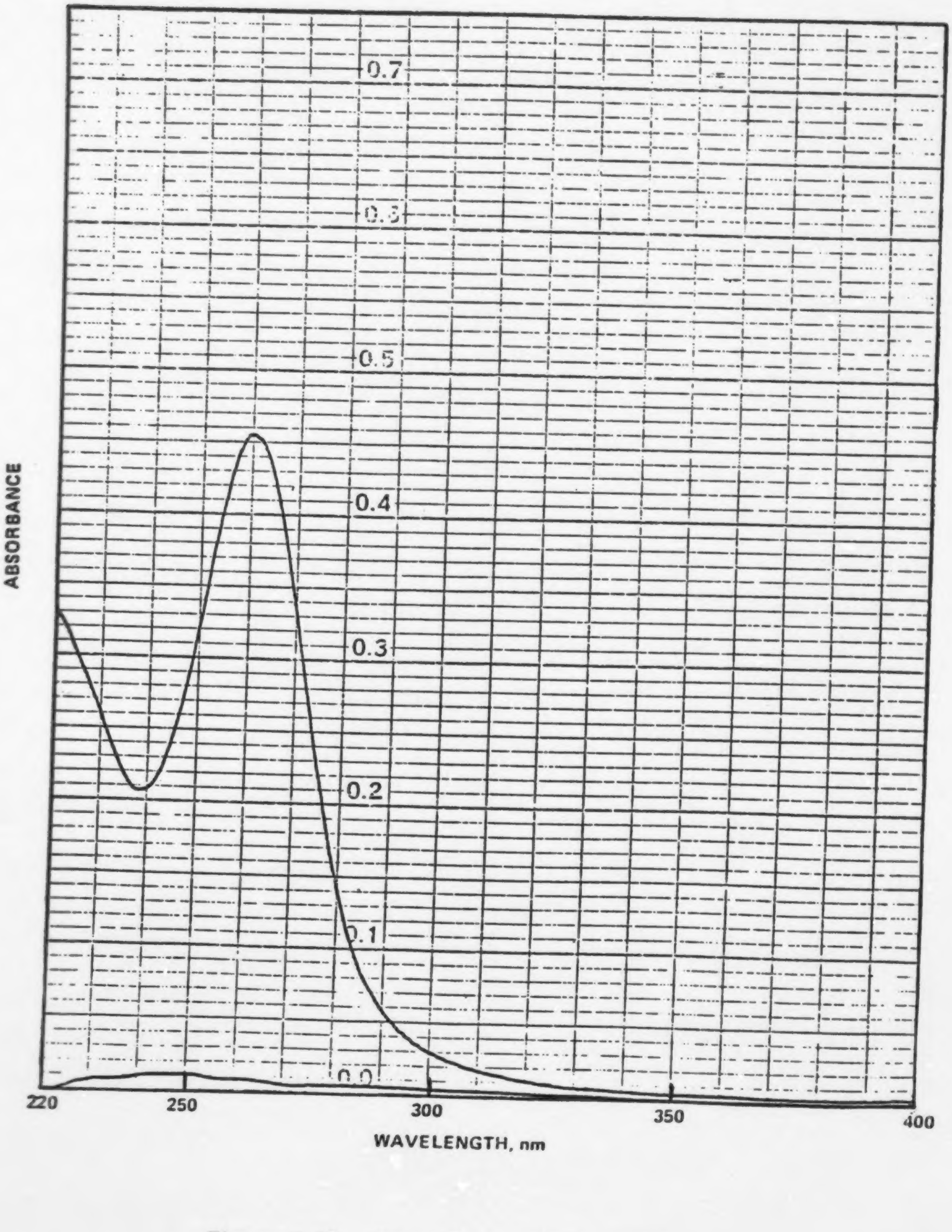


Figure C-69. UV spectrum of selenourea.

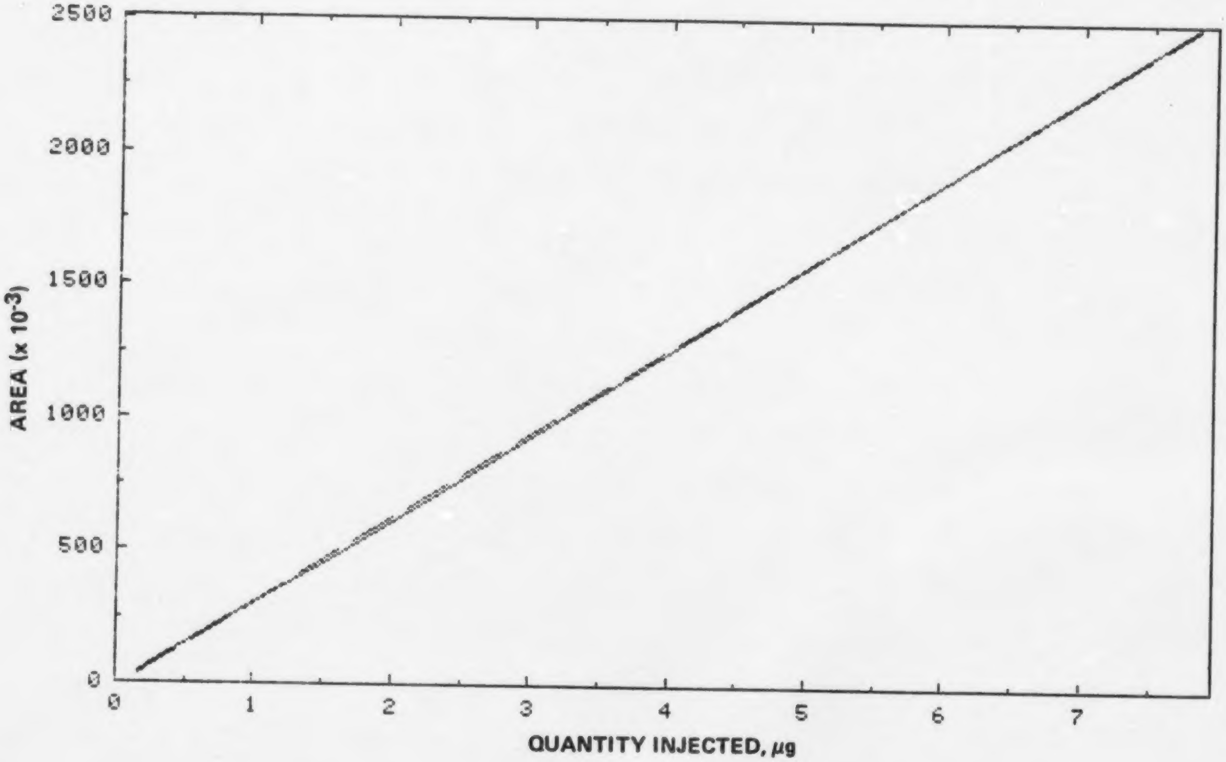


Figure C-70. Calibration curve for the determination of selenourea by HPLC/UV.

Range: 0.2-8 μg
Correlation coefficient: 0.999
Slope: 3.21×10^{2}
y-Intercept: -1.80×10^{1}

APPENDIX D

CHROMATOGRAMS AND CALIBRATION CURVES FOR HPLC/FLUORESCENCE DETERMINATIONS

Index

Compound	Reference chromatogram Figure No.	Reference calibration curve Figure No.
Aflatoxin B-1	D-1	D-3
Aflatoxin B-2	D-4	D-6
Aflatoxin G-1	D-1	D-2
Aflatoxin G-2	D-4	D-5
Benz(a)anthracene	D-7	D-8
Benzo(b)fluoranthene	D-9	D-10
Benzo(a)pyrene	D-11	D-12
Dibenz(a,j)acridine	D-13	D-14
Dibenz(a,h)anthracene	D-15	D-16
7,12-Dimethylbenz(a)anthracene	D-17	D-18
Fluoranthene	D-19	D-20
Indeno(1,2,3-c,d)pyrene	D-21	D-22
3-Methylcholanthrene	D-23	D-24

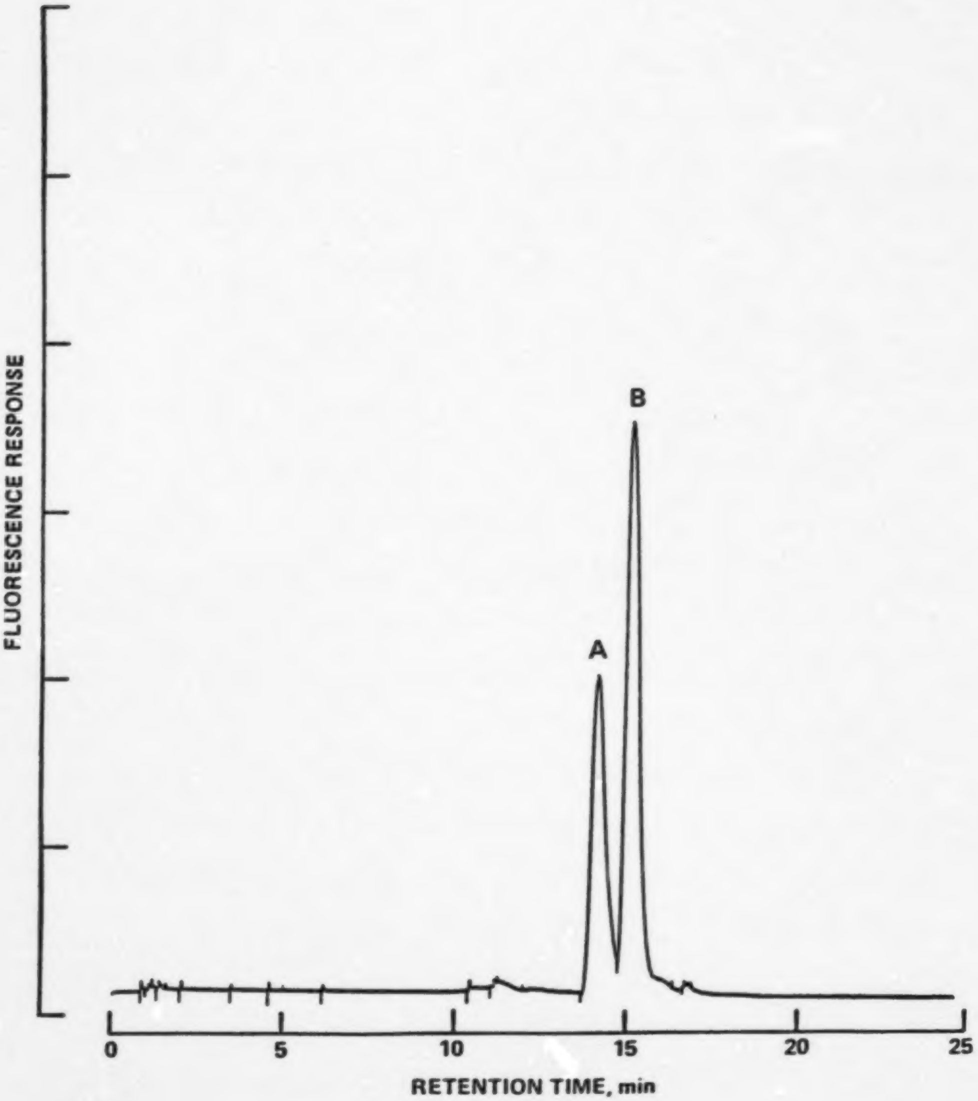


Figure D-1. Chromatogram by HPLC/Fluorescence for:

(A) Aflatoxin G-1,
(B) Aflatoxin B-1.

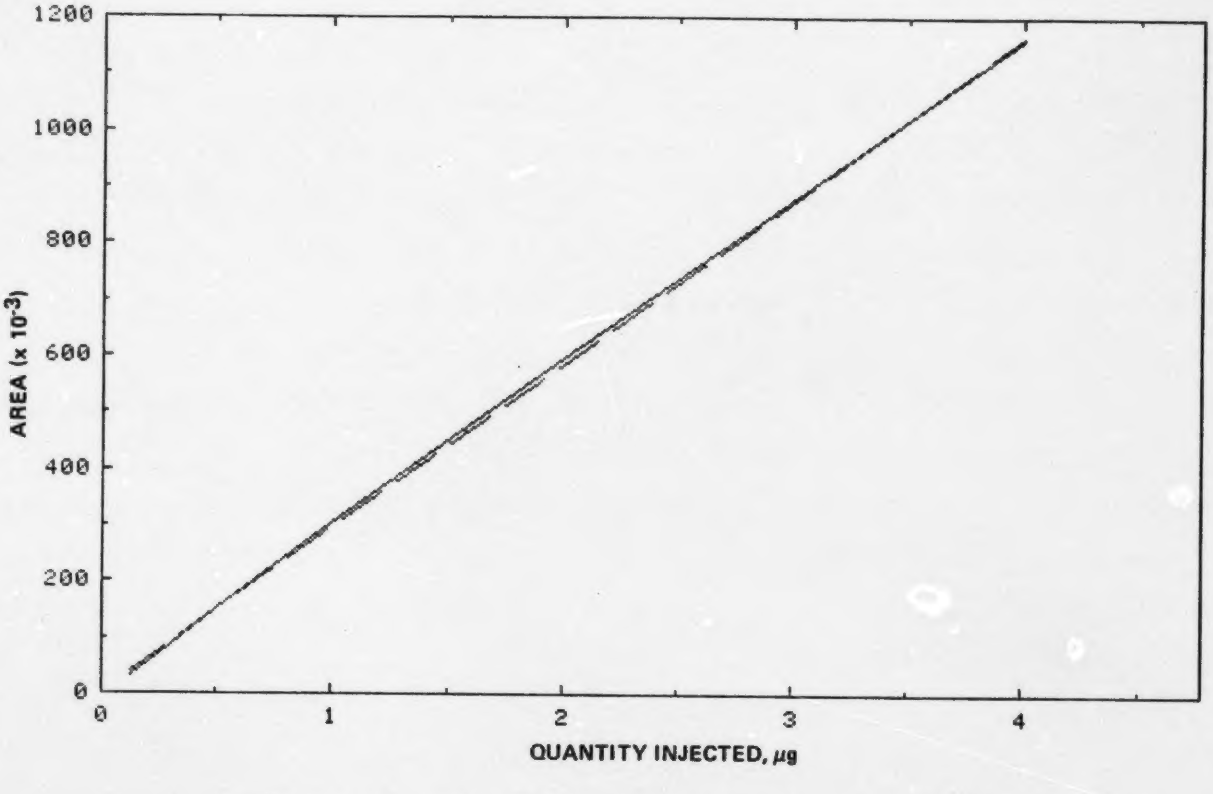


Figure D-2. Calibration curve for the determination of aflatoxin G-1 by HPLC/Fluorescence.

Range: 0.02-4 μg
Correlation coefficient: 0.999
Slope: 2.90 x 10^2
y-Intercept: 4.09

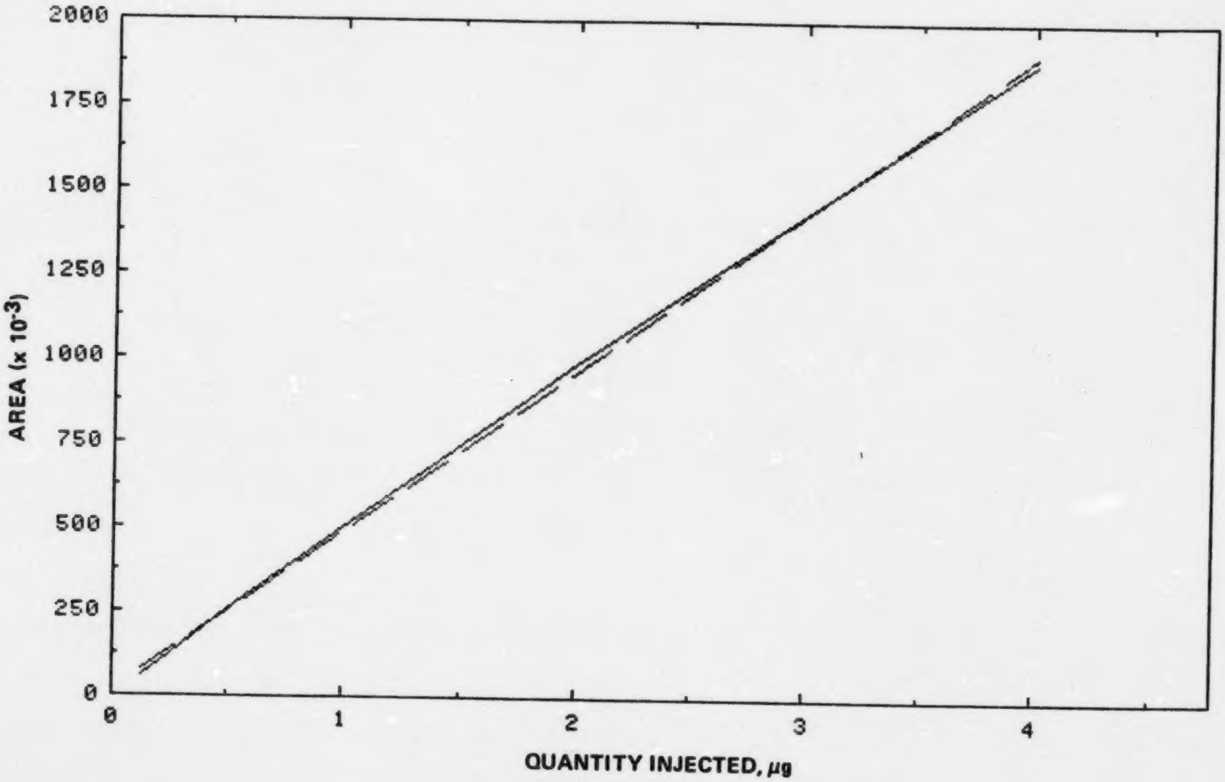


Figure D-3. Calibration curve for the determination of aflatoxin B-1 by HPLC/Fluorescence.

Range: 0.1-4 μg
Correlation coefficient: 0.999
Slope: 4.70×10^2
y-Intercept: 1.81×10^1

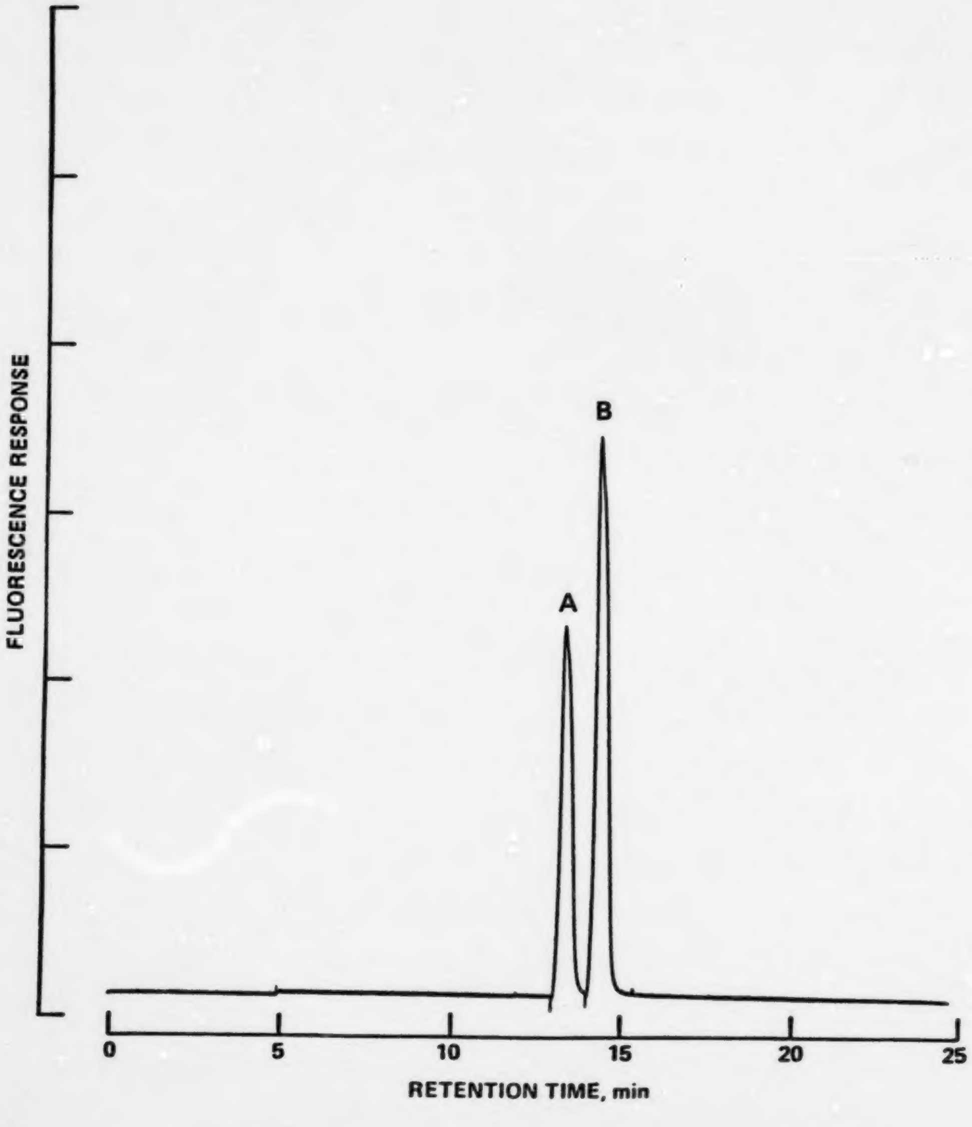


Figure D-4. Chromatogram by HPLC/Fluorescence for:

(A) Aflatoxin G-2,
(B) Aflatoxin B-2.

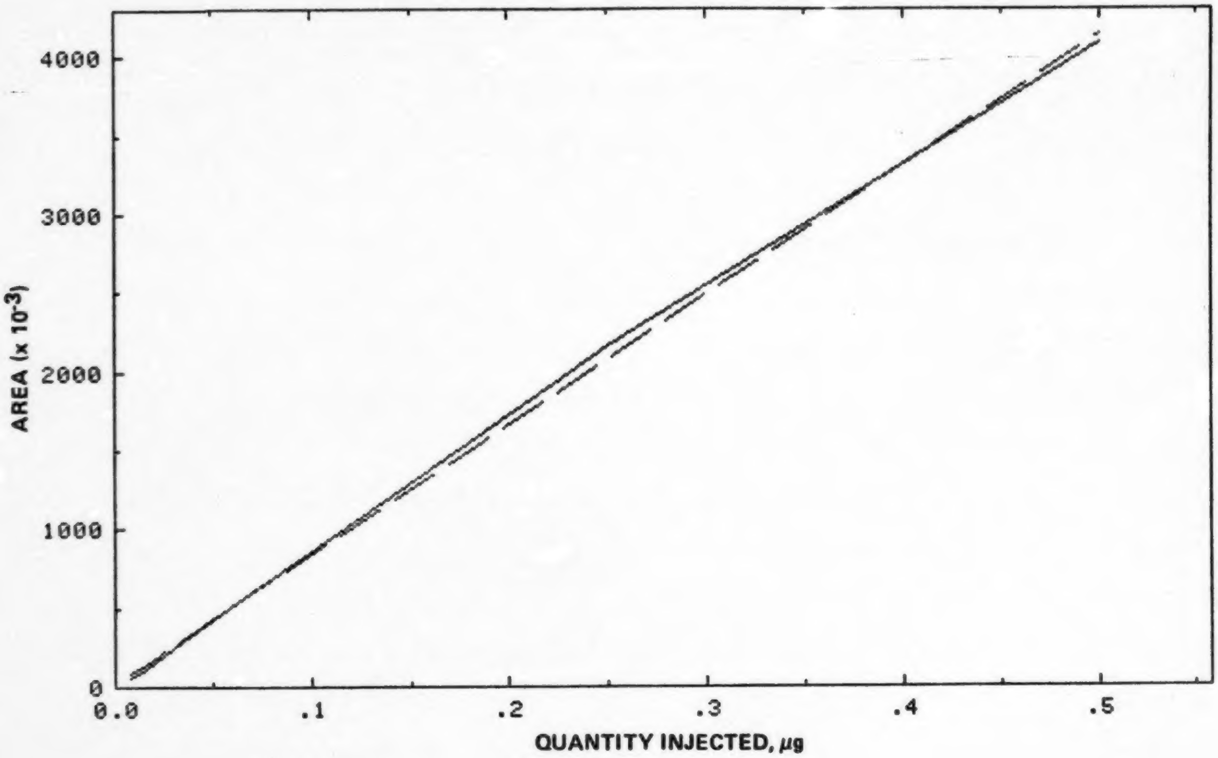


Figure D-5. Calibration curve for the determination of aflatoxin G-2 by HPLC/Fluorescence.

Range: 0.005-0.5 µg
Correlation coefficient: 0.999
Slope: 8.24×10^3
y-Intercept: 1.70×10^1

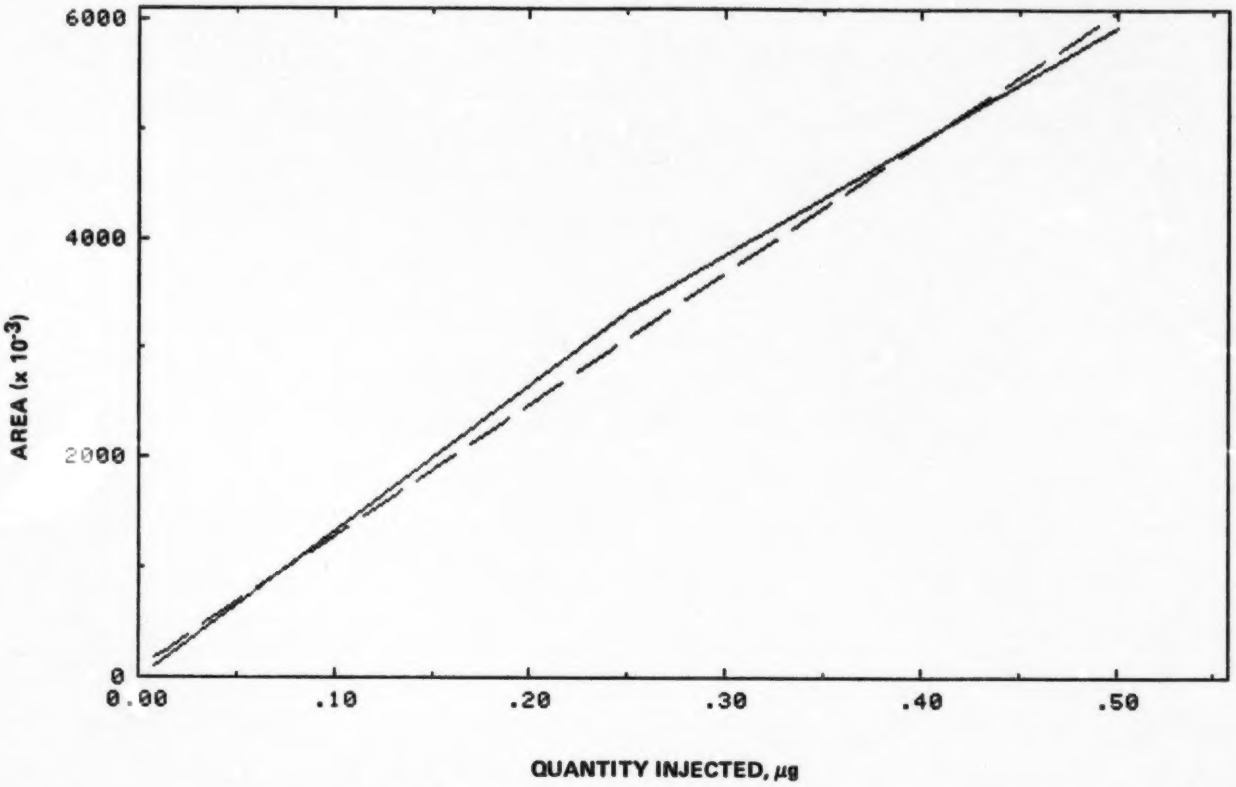


Figure D-6. Calibration curve for the determination of aflatoxin B-2 by HPLC/Fluorescence.

Range: 0.02-.5 µg
Correlation coefficient: 0.998
Slope: 1.20×10^4
y-Intercept: 8.00×10^1

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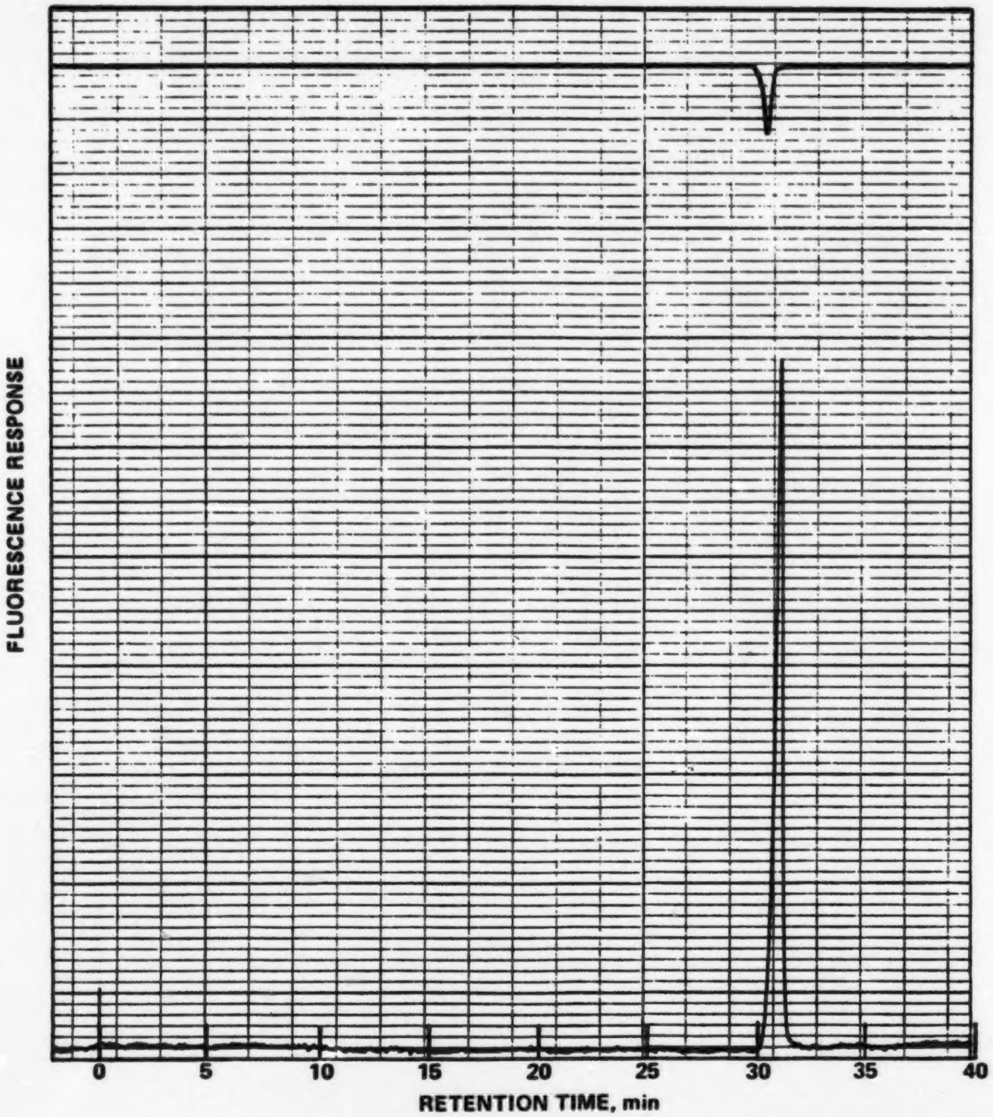

Figure D-7. Chromatogram by HPLC/Fluorescence for benz(a)anthracene.

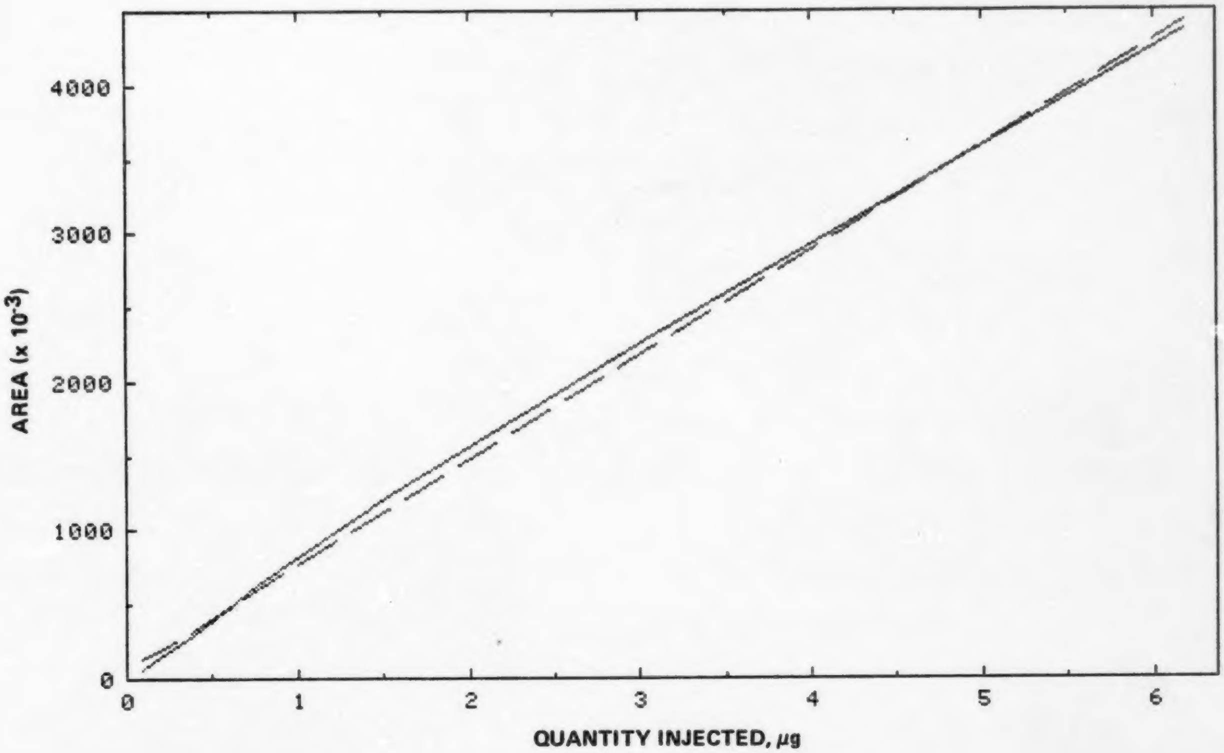

Figure D-8. Calibration curve for the determination of benz(a)anthracene by HPLC/Fluorescence.

Range: 0.2-6 µg
Correlation coefficient: 0.999
Slope: 7.06×10^2
y-Intercept: 5.77×10^1

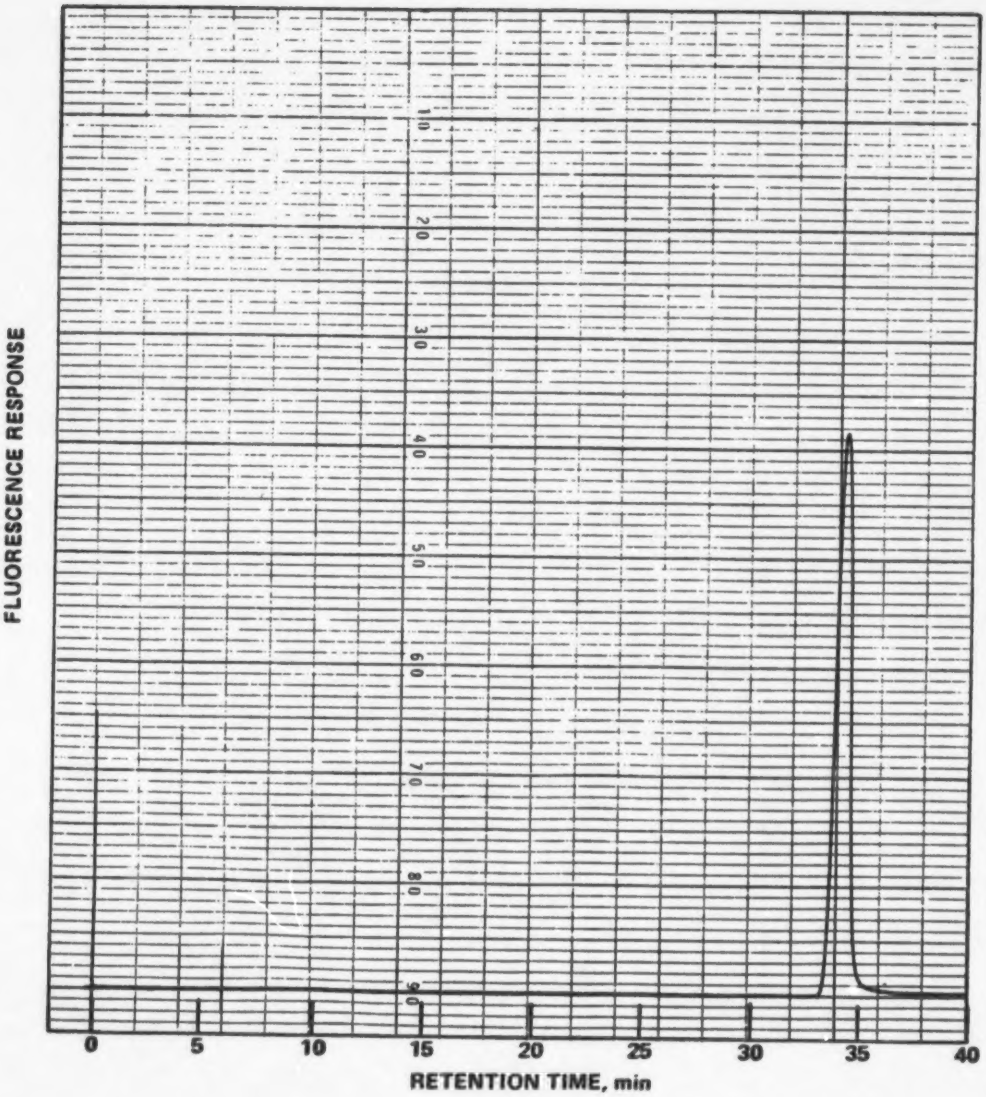

Figure D-9. Chromatogram by HPLC/Fluorescence for benzo(b)fluoranthene.

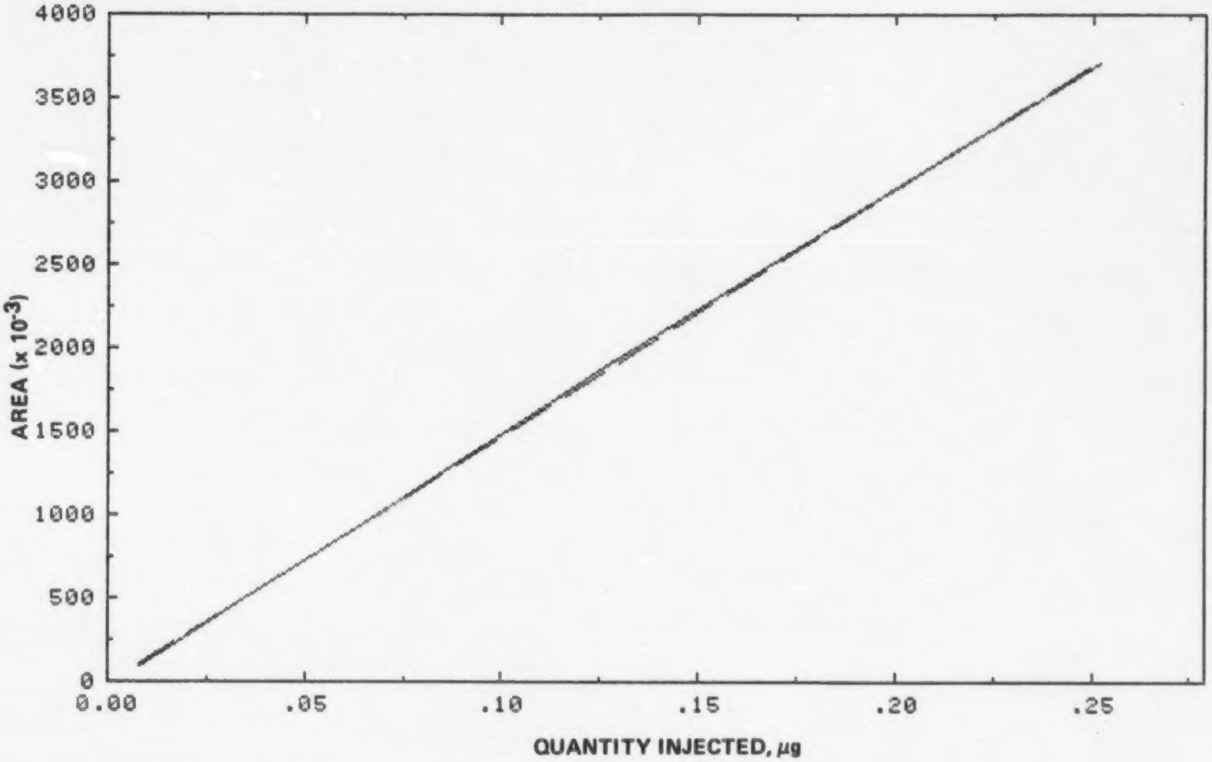

Figure D-10. Calibration curve for the determination of benzo(b)fluoranthene by HPLC/Fluorescence.

Range: 0.001-0.250 µg
Correlation coefficient: 0.999
Slope: 1.48×10^4
y-Intercept: -1.44×10^1

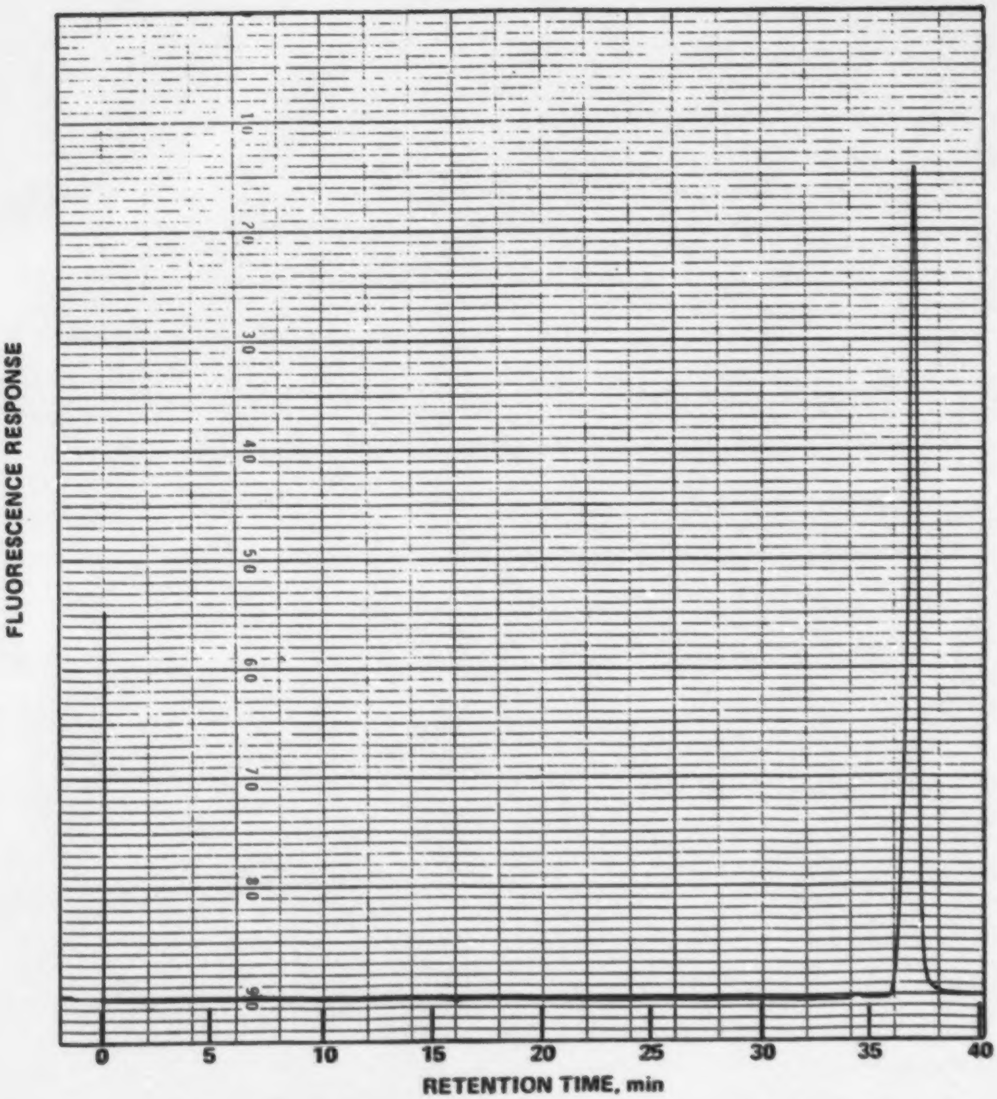

Figure D-11. Chromatogram by HPLC/Fluorescence for benzo(a)pyrene.

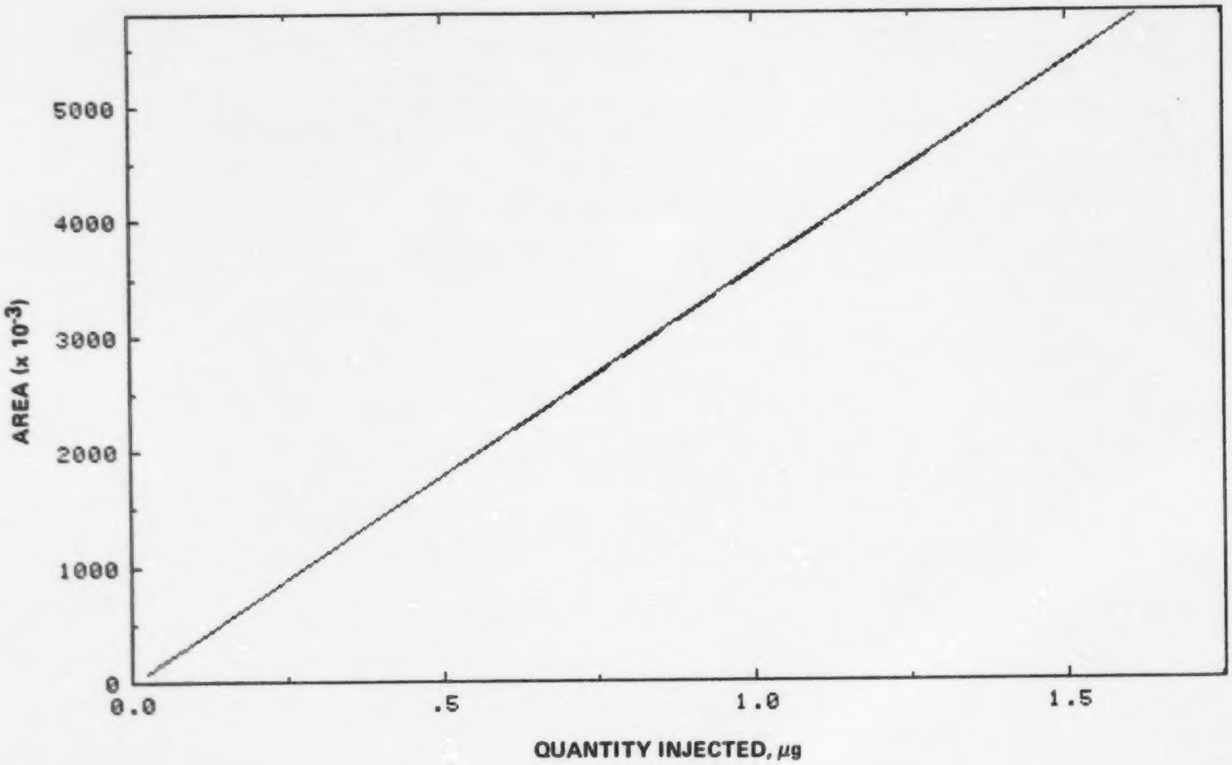

Figure D-12. Calibration curve for the determination of benzo(a)pyrene by HPLC/Fluorescence.

Range: 0.01-1.6 μg
Correlation coefficient: 0.999
Slope: 3.58×10^3
y-Intercept: -1.58×10^1

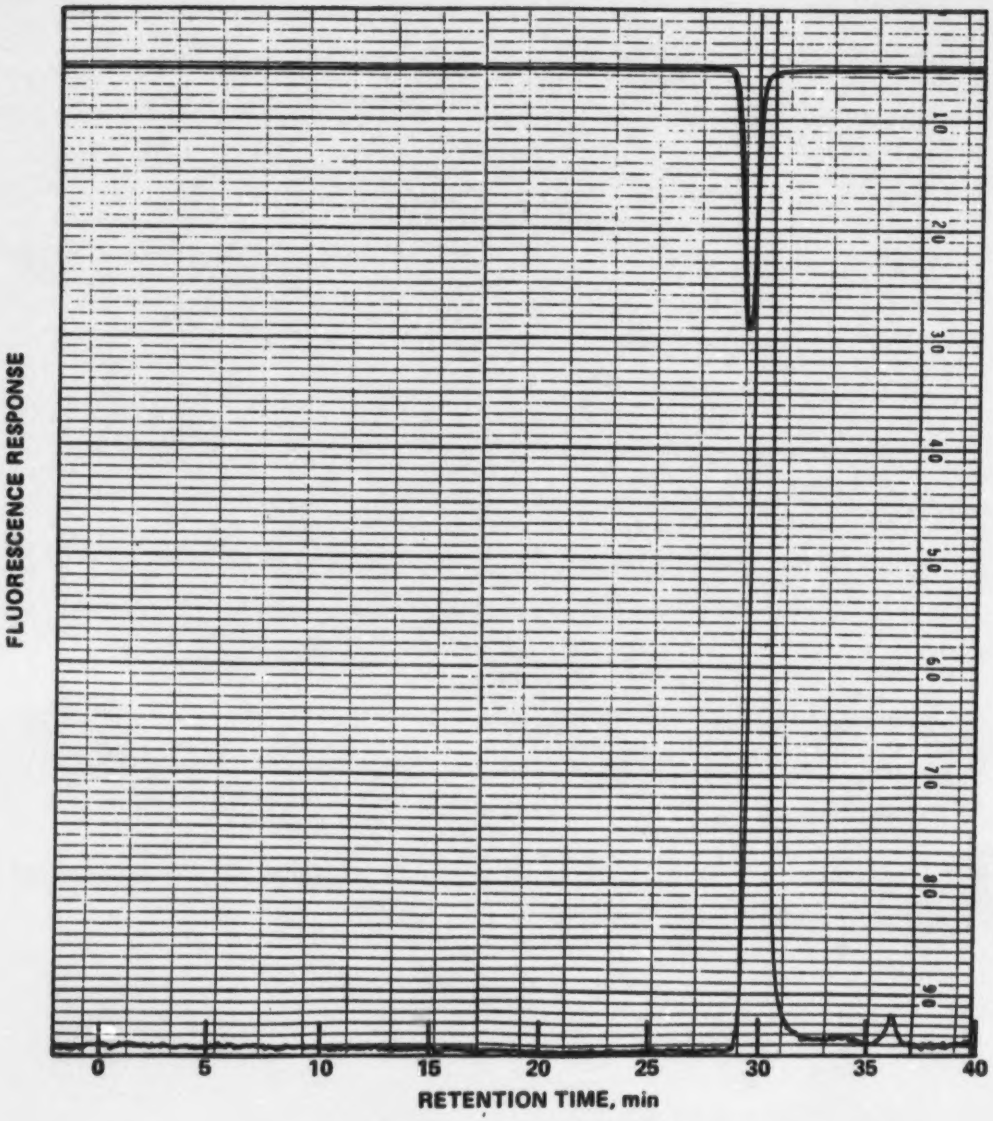

Figure D-13. Chromatogram by HPLC/Fluorescence for dibenz(a,j)acridine.

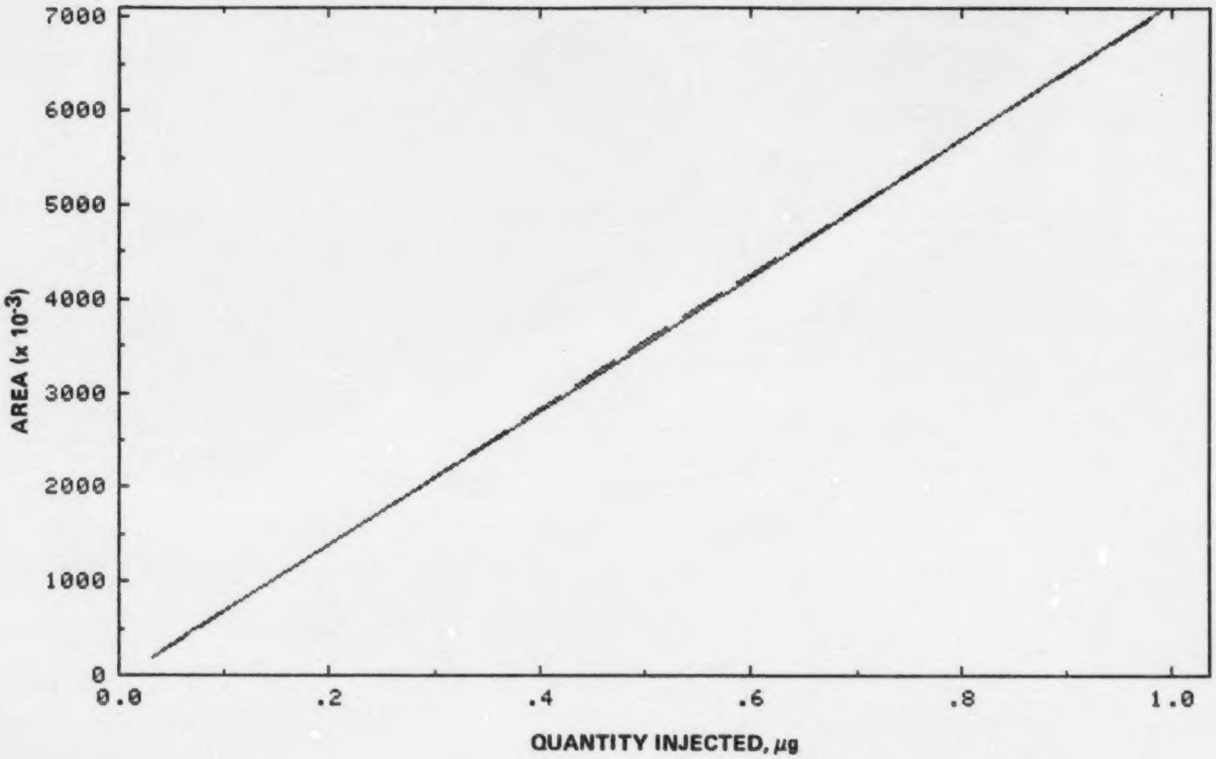

Figure D-14. Calibration curve for the determination of dibenz(a,j)acridine by HPLC/Fluorescence.

Range: 0.02-1 μg
Correlation coefficient: 0.999
Slope: 7.18×10^3
y-Intercept: -3.78×10^1

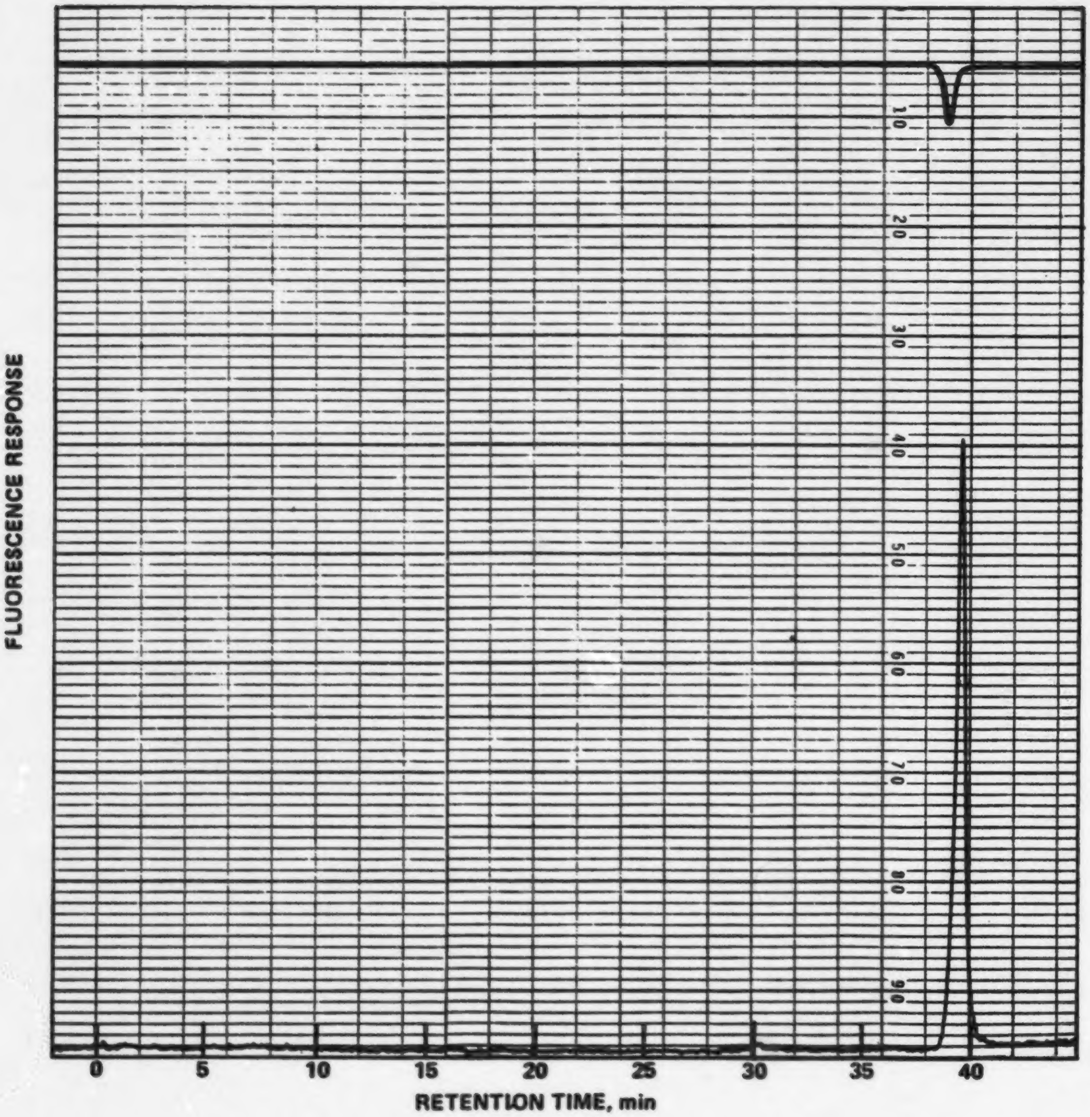

Figure D-15. Chromatogram by HPLC/Fluorescence for dibenz(a,h)anthracene.

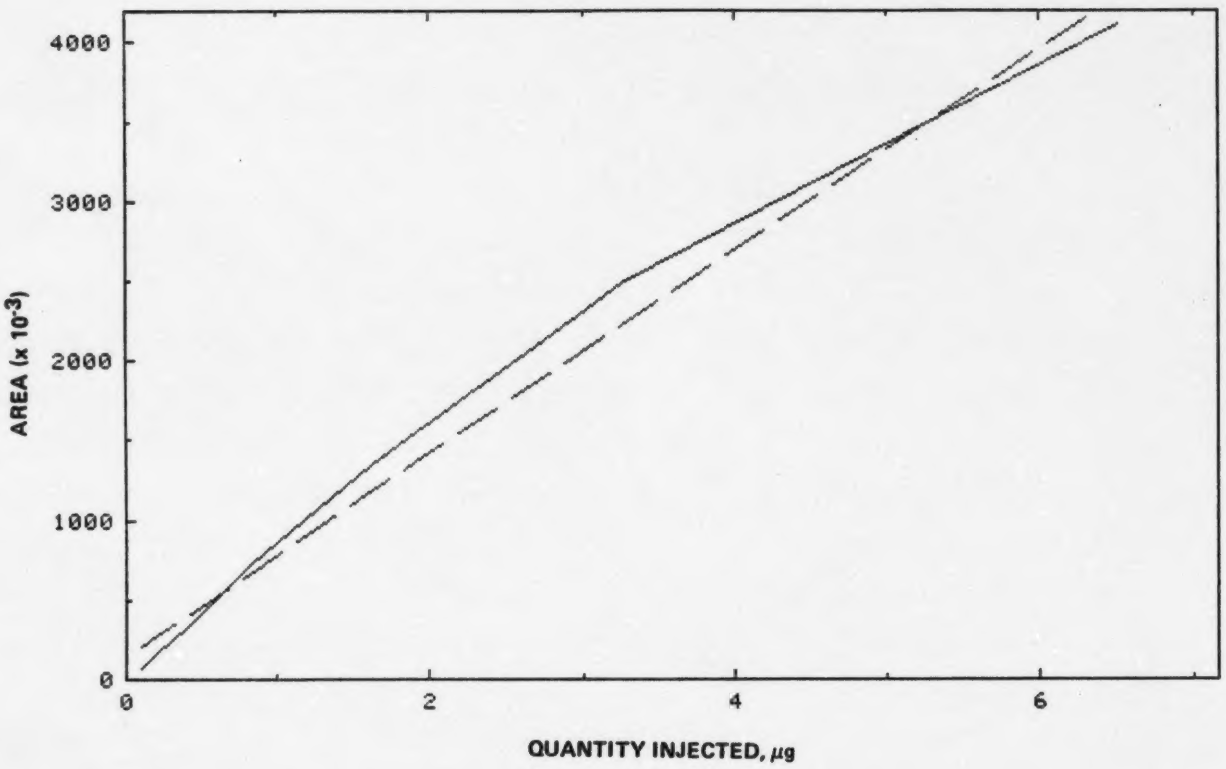

Figure D-16. Calibration curve for the determination of dibenz(a,h)anthracene by HPLC/Fluorescence.

Range: 0.4-6 μg
Correlation coefficient: 0.994
Slope: 6.37×10^2
y-Intercept: 1.45×10^2

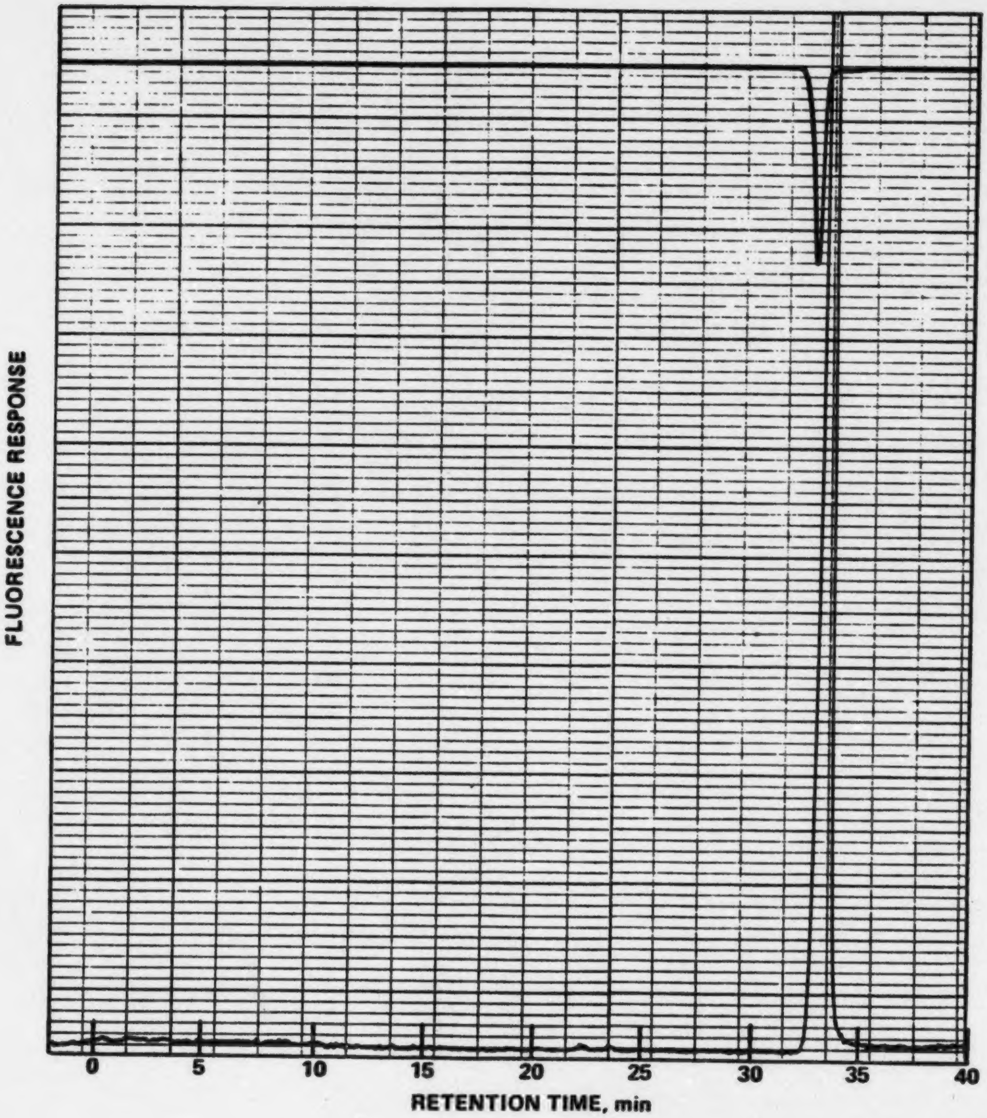

Figure D-17. Chromatogram by HPLC/Fluorescence for 7,12-dimethylbenz(a)anthracene.

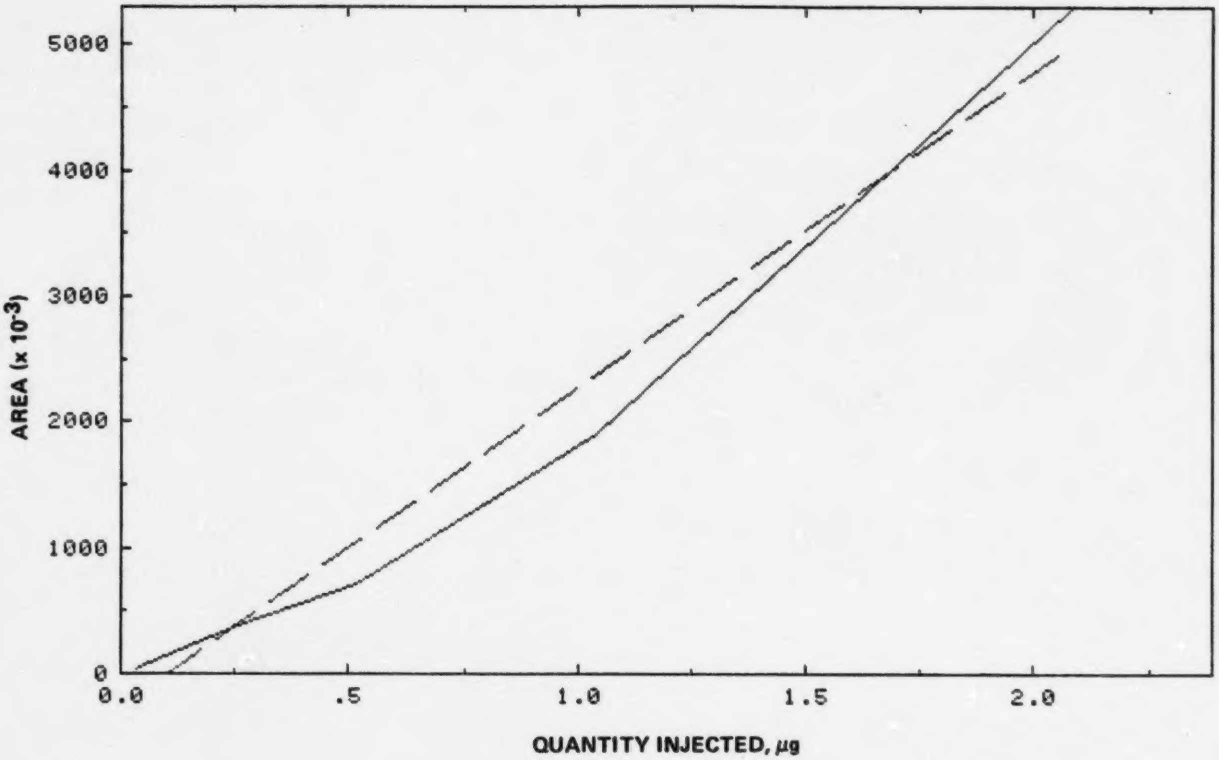

Figure D-18. Calibration curve for the determination of 7,12-dimethylbenz(a)anthracene by HPLC/ Fluorescence.

Range: 0.03-2 µg
Correlation coefficient: 0.988
Slope: 2.52×10^3
y-Intercept: -2.55×10^2

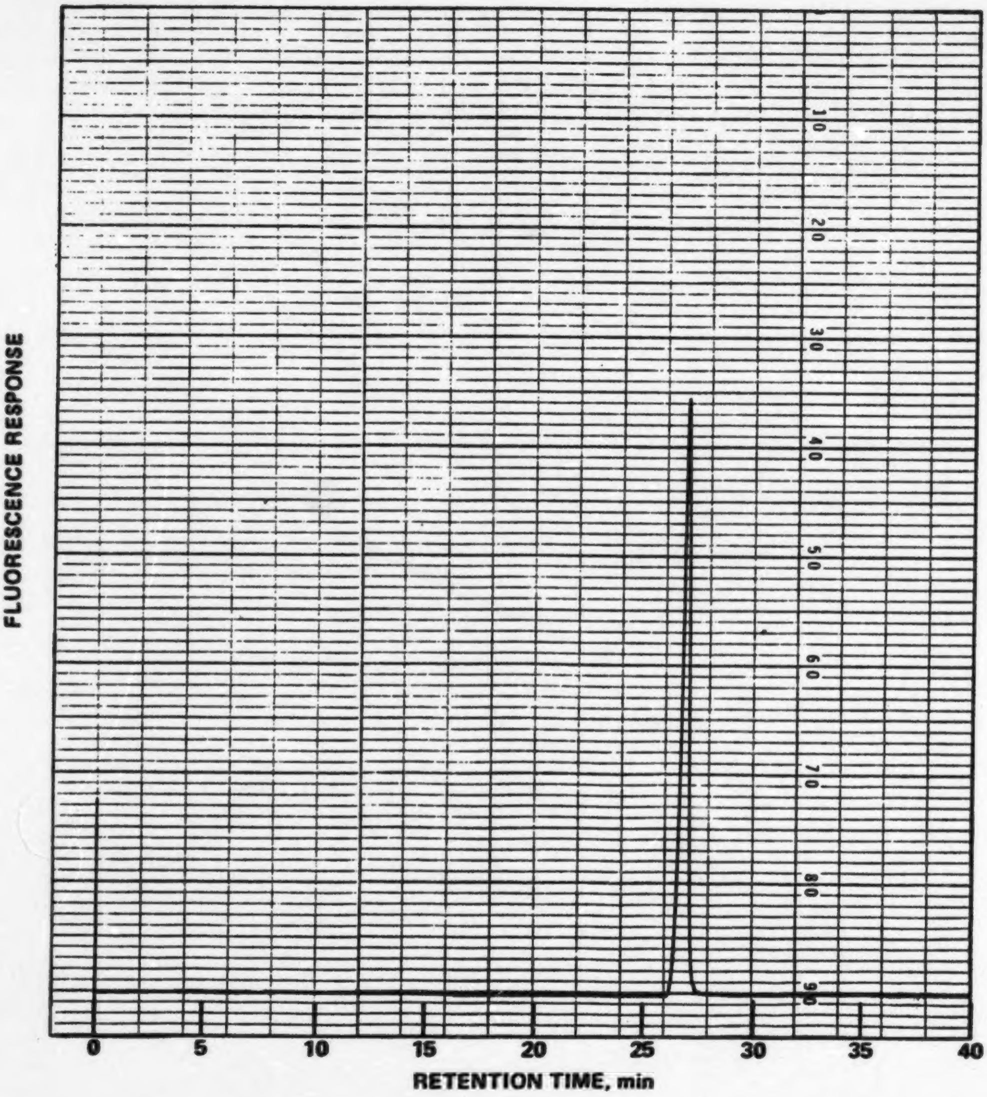

Figure D-19. Chromatogram by HPLC/Fluorescence for fluoranthene.

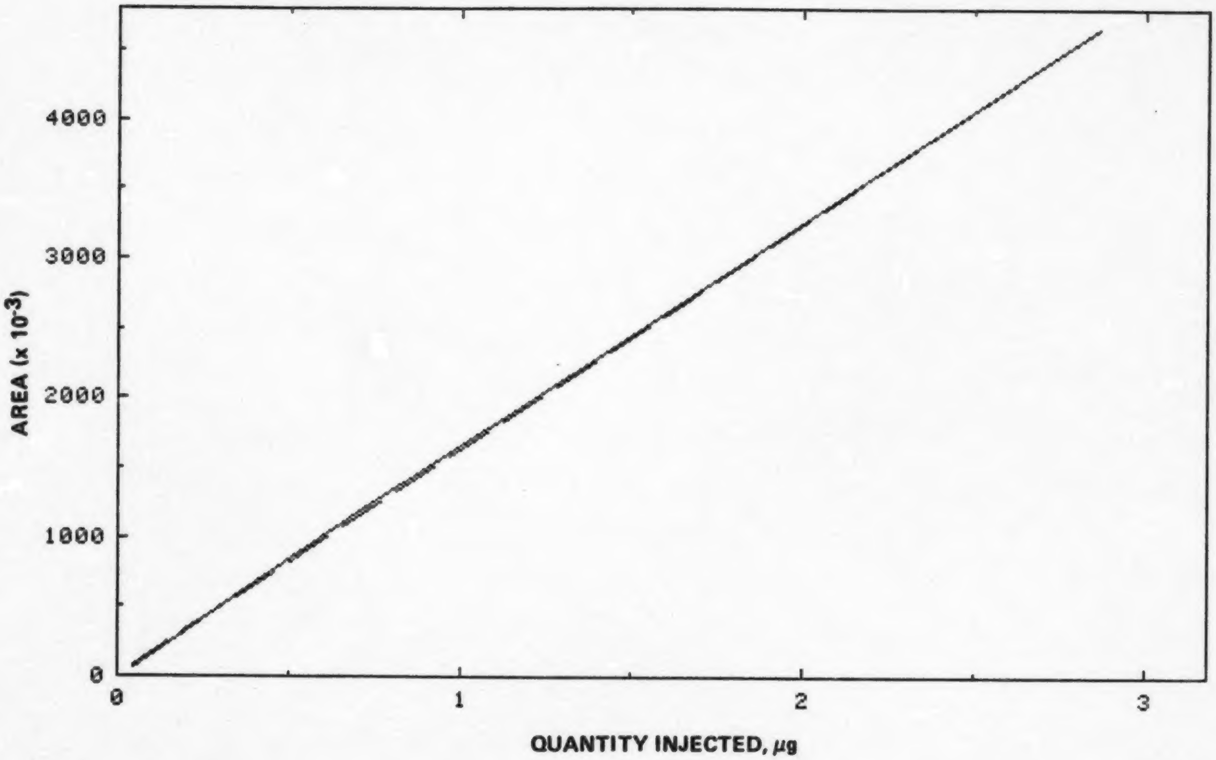

Figure D-20. Calibration curve for the determination of fluoranthene by HPLC/Fluorescence.

Range: 0.02-3 μg
Correlation coefficient: 0.999
Slope: 1.62×10^3
y-Intercept: 6.71

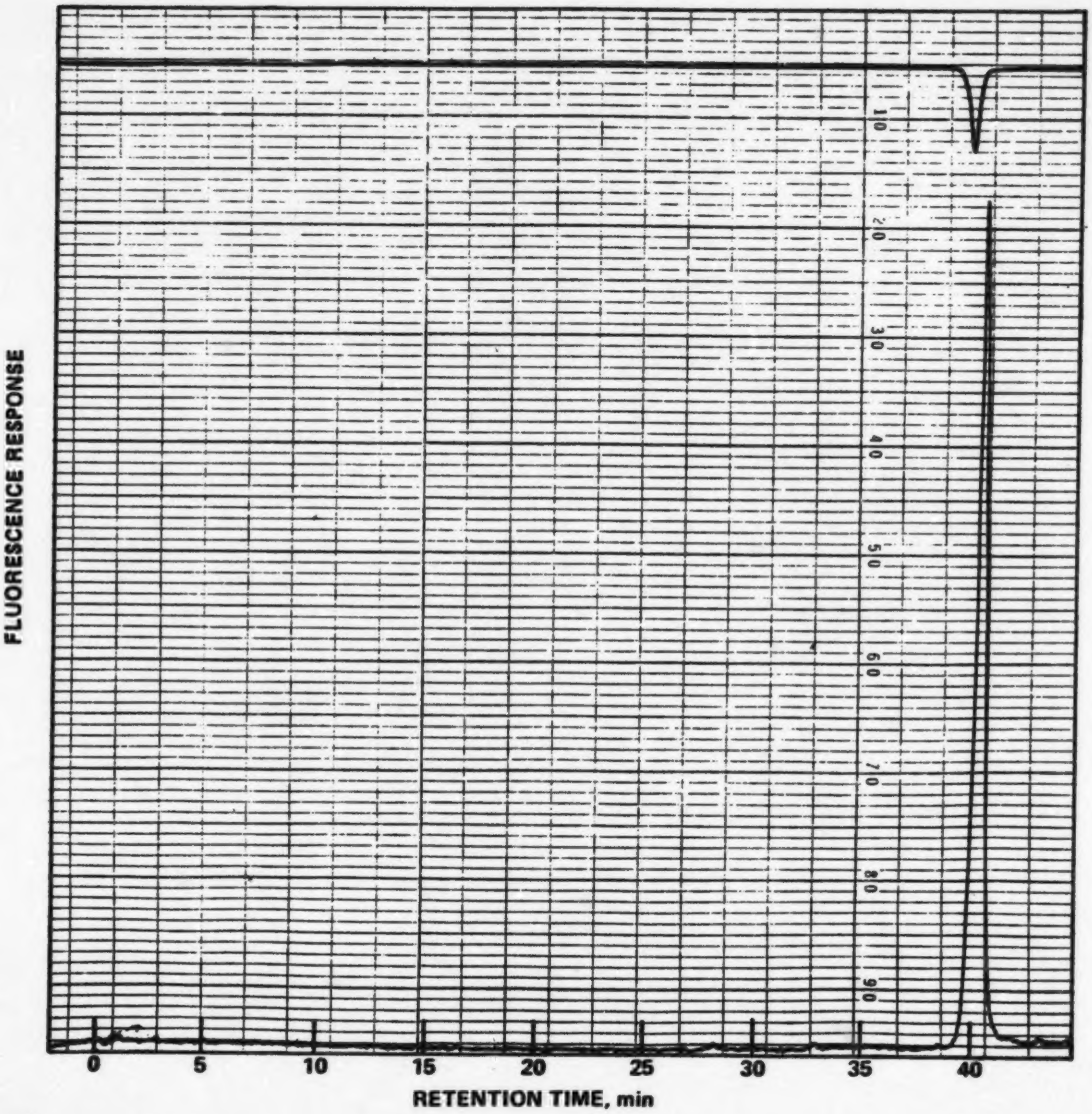

Figure D-21. Chromatogram by HPLC/Fluorescence for indeno(1,2,3-c,d)pyrene.

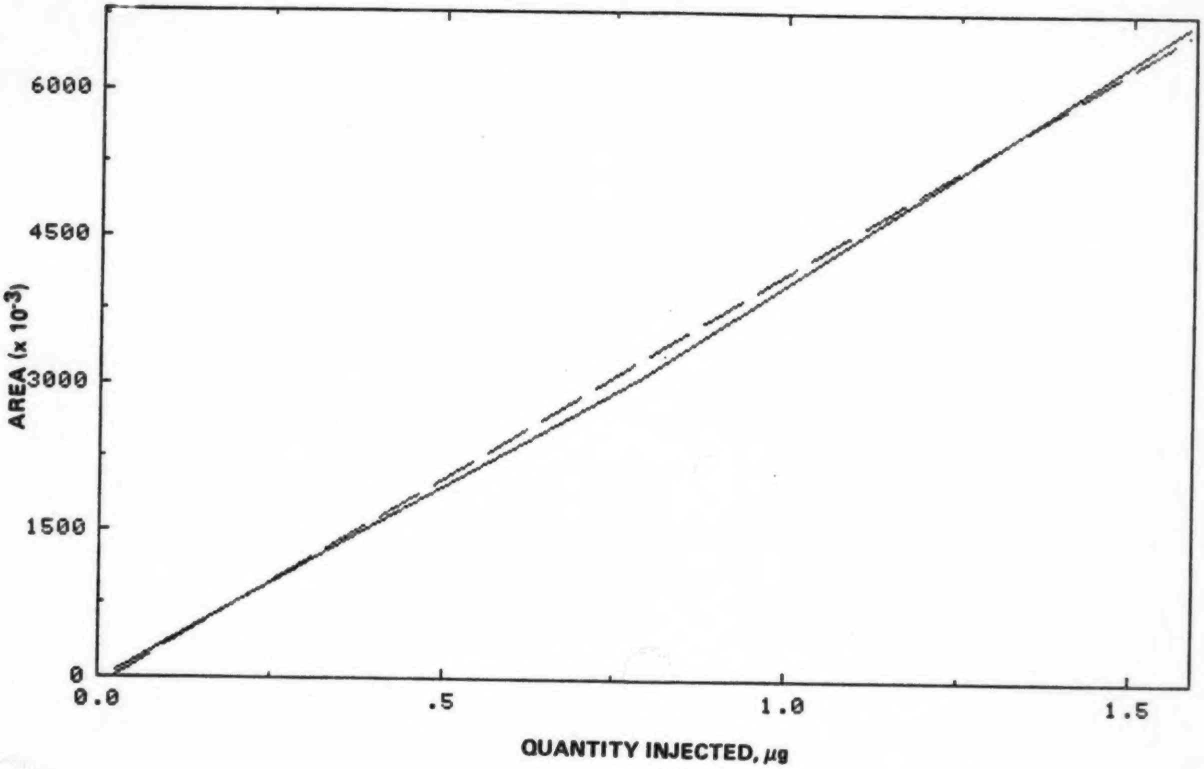

Figure D-22. Calibration curve for the determination of indeno(1,2,3-c,d)pyrene by HPLC/Fluorescence.

Range: 0.02-1.5 μg
Correlation coefficient: 0.999
Slope: 4.23×10^3
y-Intercept: -8.75×10^1

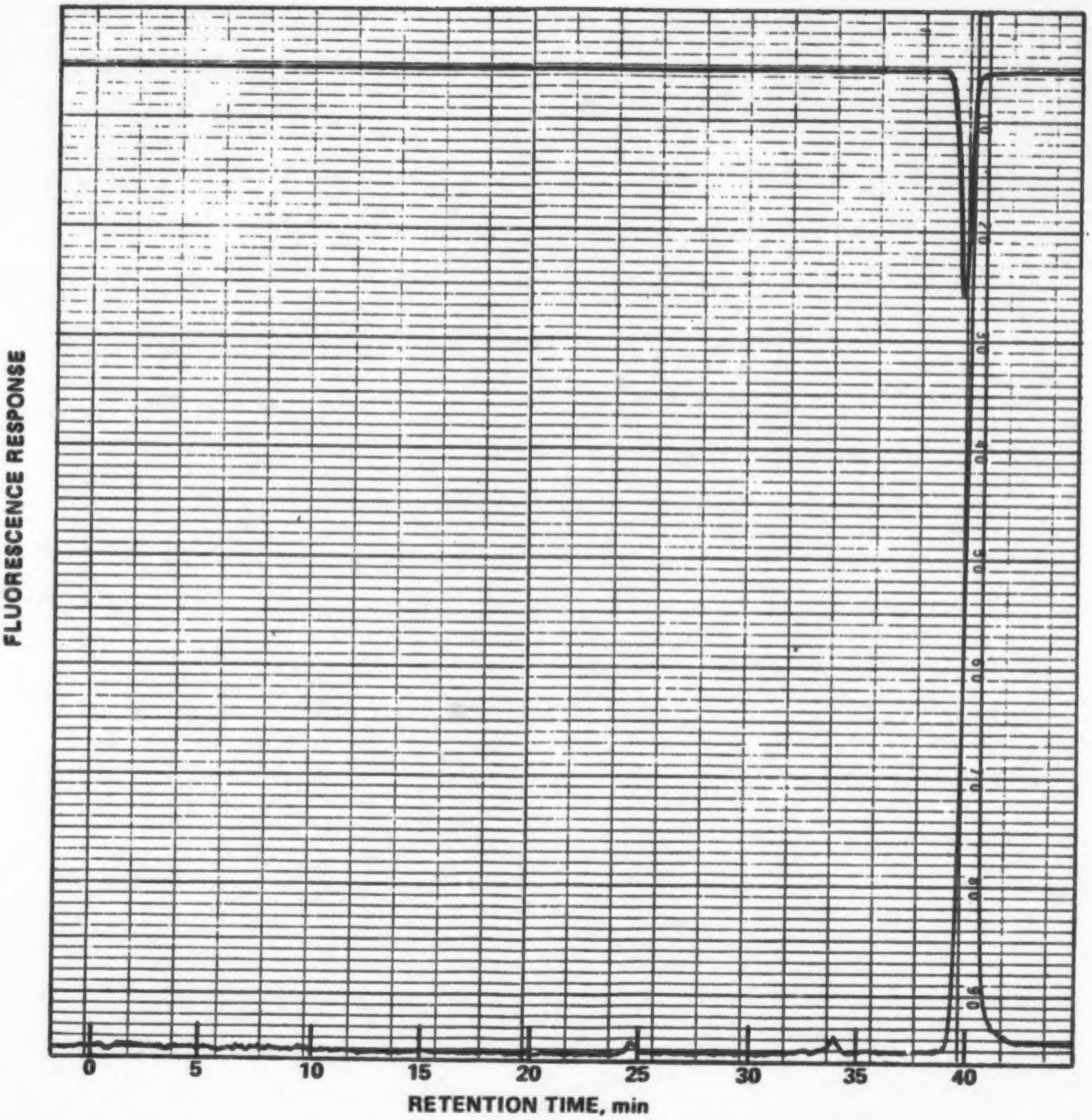

Figure D-23. Chromatogram by HPLC/Fluorescence for 3-methylcholanthrene.

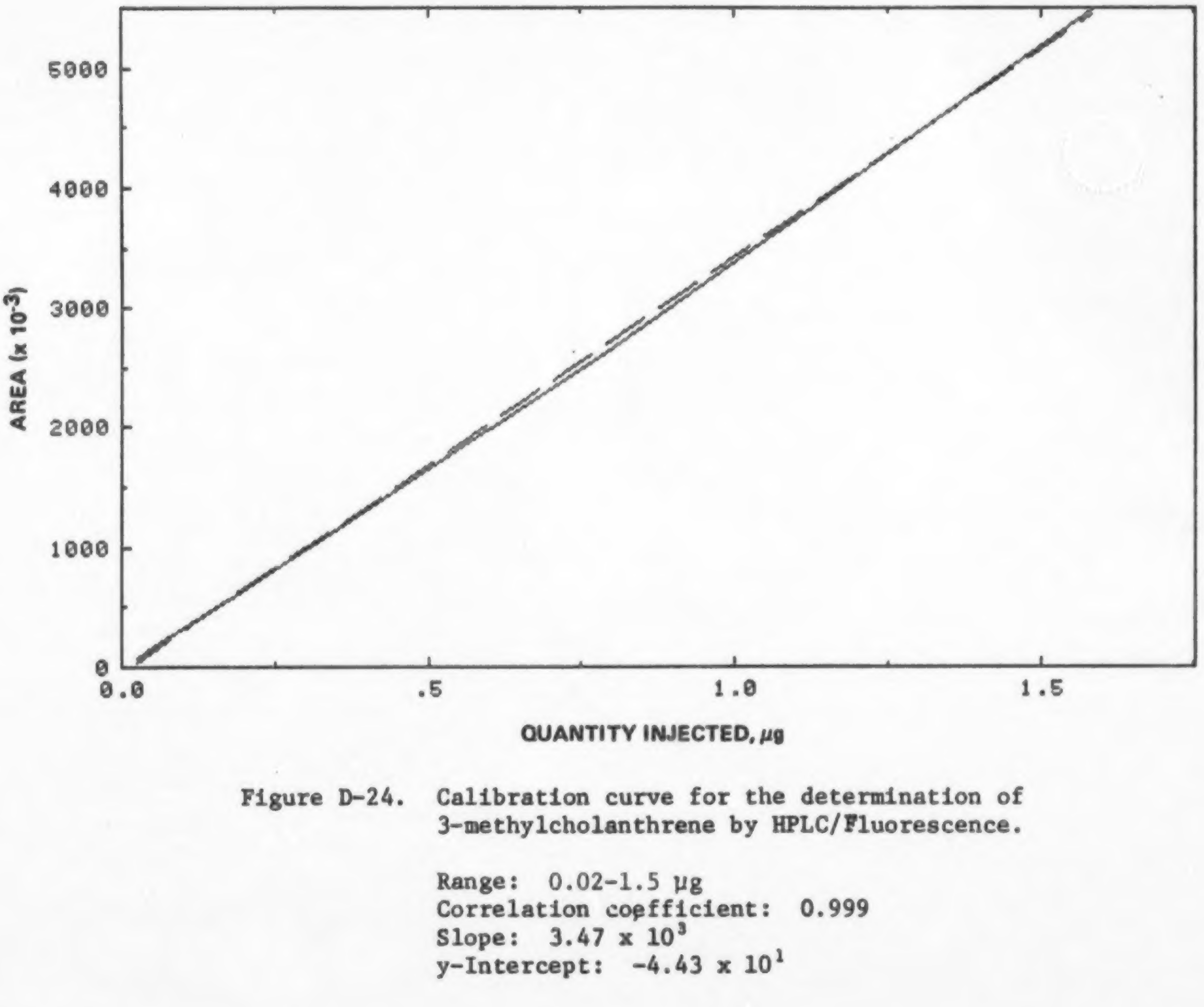

Figure D-24. Calibration curve for the determination of 3-methylcholanthrene by HPLC/Fluorescence.

Range: 0.02-1.5 µg
Correlation coefficient: 0.999
Slope: 3.47×10^3
y-Intercept: -4.43×10^1